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Published in:
Journal of Chemical Physics

DOI:
10.1063/1.1568333

Publication date:
2003

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Citation: J. Chem. Phys. **118**, 9109 (2003); doi: 10.1063/1.1568333
View online: https://doi.org/10.1063/1.1568333
View Table of Contents: http://aip.scitation.org/toc/jcp/118/20
Published by the American Institute of Physics

Microscopic derivation of hydrodynamic equations for phase-separating fluid mixtures

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(Received 13 January 2003; accepted 25 February 2003)

The hydrodynamic equations of a phase-separating fluid mixture are derived from the underlying microscopic dynamics of the system. A projection operator method is used in the GENERIC form [H. C. Öttinger, Phys. Rev. E **57**, 1416 (1998)]. In this way, the thermodynamic consistency of the final equations is apparent. The microscopic potential is separated into short- and long-range parts, in the spirit of the original work of van der Waals. Explicit expressions for surface tension terms in the hydrodynamic equations are obtained. These terms describe diffuse interfaces in the system. Miscible–immiscible and gas–liquid phase transitions are possible, nonisothermal situations can be studied, and explicit account of cross effects is taken. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1568333]

I. INTRODUCTION

Fluid mixtures at equilibrium may present a very rich phase diagram which increases in complexity with the number of different species. The equilibrium phase diagram is determined by the free energy of the system for which many models exist, as presented in the excellent textbook by Davis.[1] Of outstanding importance is the van der Waals model, which allows one to understand qualitatively and, sometimes, quantitatively the phase behavior of these fluid systems.[1] According to the van der Waals picture, phase transitions and surface tension effects in mixtures can be explained by assuming that the potential of interaction $\phi_{i_\alpha j_\beta}$ between molecules of species α, β can be expressed as the sum of two contributions,

$$\phi_{i_\alpha j_\beta} = \hat{\phi}^{\alpha\beta}(\mathbf{q}_{i_\alpha} - \mathbf{q}_{j_\beta}) + \overline{\phi}^{\alpha\beta}(\mathbf{q}_{i_\alpha} - \mathbf{q}_{j_\beta}). \tag{1}$$

Here, $\mathbf{q}_{i_\alpha}$ is the position of the ith molecule of species α and $\hat{\phi}^{\alpha\beta}(r) \geqslant 0$ is a short-range repulsive (hard core) part and $\overline{\phi}^{\alpha\beta}(r) \leqslant 0$ is a long-range attractive tail.[1] Realistic potentials can be decomposed usually in the above way. However, one of the assumptions in the van der Waals model is that the range of the long-range potential is *much* larger than the range of the hard core potential.[2] Although this is not the case for realistic potentials, the van der Waals picture seems to be more general than what its assumptions suggest.[2,3]

In this paper, we want to contribute to the theoretical understanding of the interplay of equilibrium phase transitions and hydrodynamics, by formulating in a thermodynamically consistent way the hydrodynamic equations of a mixture of fluids that display phase separation. Although the hydrodynamic equations for mixtures of liquids are well known and different approaches have been considered for their derivation ranging from kinetic theory,[4] microscopic derivations,[5,6] or phenomenological approaches,[7–9] what seems to be lacking is the formulation of the general hydrodynamic equations when phase transitions and surface tension effects are present. A promising approach for dealing with the dynamics of phase separating mixtures is based on the phase field method.[10] Within this context several derivations of the hydrodynamic equations for phase separating fluids have been proposed based on *phenomenological* linear irreversible thermodynamics.[10–12] We are not aware of any *microscopic* derivation of the hydrodynamics of phase-separating fluids. It will become apparent that ambiguities in the definition of the hydrodynamic variables in the phenomenological approaches can be dispelled by resorting to a microscopic derivation.

The results presented in this paper can be understood as the answer to the following question: how can the equilibrium van der Waals picture for a fluid mixture be generalized to nonequilibrium situations? To this end, we derive the hydrodynamic equations for a phase-separating mixture starting from the microscopic dynamics of the system, which is governed by a separable potential like in Eq. (1). This is achieved by calculating the microscopically defined[13] building blocks of the recently developed framework for nonequilibrium thermodynamics known as GENERIC.[14] This acronym stands for general equation for nonequilibrium reversible irreversible coupling. A similar approach has been taken for the case of a *simple fluid* without phase transitions in Ref. 15. The hydrodynamic equations of a simple fluid able to display a gas–liquid phase transition have been presented within the GENERIC framework in Ref. 16.

Due to the large number of equations required in order to obtain the final hydrodynamic equations for a mixture starting from the microscopic dynamics of the system, we present in Sec. II a summary and a discussion of the main results of the paper. This section should be sufficient for those readers

who are not interested in the detailed microscopic calculations presented in latter sections. In Sec. III, we present a summary of the GENERIC framework along with the microscopic definitions of its different building blocks. In Sec. IV, we present the detailed calculation of these microscopically defined building blocks for the particular case of a mixture of fluids.

II. HYDRODYNAMIC EQUATIONS

In this section, we summarize the main results of this paper. The state x of a fluid mixture of r species is described by the set of hydrodynamic variables, that is, the number density $n_{\mathbf{r}}^{\alpha}$ of species α, with $\alpha=1,\ldots,r$, the momentum density $\mathbf{g}_{\mathbf{r}}$ of the full mixture, and the internal energy density $\hat{\epsilon}_{\mathbf{r}}$, which are defined in terms of molecular coordinates and momenta in Eqs. (75) in Sec. IV. It is important to note that the molecular definition of the internal energy density field contains only the short-range part $\hat{\phi}$ of the potential of Eq. (1). In this way, the total energy of the system written in terms of the hydrodynamic variables is given by

$$E[x]=\int d\mathbf{r}\left(\frac{\mathbf{g}_{\mathbf{r}}^2}{2\rho_{\mathbf{r}}}+\hat{\epsilon}_{\mathbf{r}}\right)+\overline{\Phi}, \tag{2}$$

where we have introduced the total mass density field as

$$\rho_{\mathbf{r}}=\sum_{\alpha}^{r} m_{\alpha} n_{\mathbf{r}}^{\alpha} \tag{3}$$

and the contribution $\overline{\Phi}$ due to the long-range part of the potential defined by

$$\overline{\Phi}=\frac{1}{2}\sum_{\alpha\beta}\int d\mathbf{r}\, d\mathbf{r}'\, n_{\mathbf{r}}^{\alpha} n_{\mathbf{r}'}^{\beta}\overline{\phi}^{\alpha\beta}(\mathbf{r}-\mathbf{r}'), \tag{4}$$

where $\overline{\phi}^{\alpha\beta}(\mathbf{r}-\mathbf{r}')$ is the long-range part of the potential of interaction between two molecules of species α and β located at $\mathbf{r}$ and $\mathbf{r}'$, respectively. This long-range potential energy is a quadratic functional of the density fields. We recognize in Eq. (2) the three contributions to the total energy of the fluid due to the kinetic energy of the fluid, the internal energy due to the hard-core part of the potential, and the final contribution due to the long-range part of the potential. In this paper, variables with a caret such as $\hat{A}$ will refer to the hard-core potential whereas variables with an overline such as $\overline{A}$ will refer to the long-range potential.

The energy functional (2) is one of the building blocks of the GENERIC framework, as summarized in Sec. III. Another building block is the entropy functional. Even though the equilibrium properties of an inhomogeneous fluid mixture can be fully understood from the *free energy functional* of the system, when considering inhomogeneous nonisothermal situations it is necessary to deal with *entropy functional* of the fluid mixture. By following the pioneering ideas of Green[6] and van Kampen,[17] we compute in Sec. IV B the entropy functional of a fluid mixture under the van der Waals approximation. Green computed the entropy of a simple fluid by assuming that the little cells in which the fluid is divided are essentially noninteracting, thus precluding the description of surface tension.[6] On the other hand, van Kampen derived the free energy functional for the van der Waals fluid with the possibility of describing surface tension effects, albeit for isothermal situations only.[17]

The entropy functional in the van der Waals approximation has the following form for a binary mixture of species A,B:

$$S[x]=\int d\mathbf{r}\hat{s}(n_{\mathbf{r}}^{A},n_{\mathbf{r}}^{B},\hat{\epsilon}_{\mathbf{r}}), \tag{5}$$

where $\hat{s}(n^A,n^B,\hat{\epsilon})$ is the entropy density function of a system of A and B molecules *which are interacting with only the short-range part of the potential* $\hat{\phi}^{\alpha\beta}$, as a function of the densities n^A and n^B and the internal energy $\hat{\epsilon}$. That the entropy functional contains only the short-range part of the potential is a nontrivial result that follows from the van der Waals assumption (see Sec. IV B). We will not need in this paper the actual functional form of $\hat{s}(n^A,n^B,\hat{\epsilon})$. The original ideas of van der Waals suggest to use a simple excluded volume model, but more sophisticated expressions for hard-core fluid mixtures can certainly be used.

The main result of this paper is the following set of hydrodynamic equations for a fluid mixture:

$$\begin{aligned}
\partial_t n^{\alpha} &= -\nabla\mathbf{v}n^{\alpha}+\nabla\left(\sum_{\beta} D^{\alpha\beta}\hat{T}\nabla\left(\frac{\hat{\mu}^{\beta}}{\hat{T}}\right)\right)\\
&\quad -\nabla\left(S^{\alpha}\hat{T}^2\nabla\left(\frac{1}{\hat{T}}\right)\right)-\nabla\left(\sum_{\beta} D^{\alpha\beta}\overline{\mathbf{F}}^{\beta}\right),\\
\partial_t\mathbf{g} &= -\boldsymbol{\nabla}\cdot(\mathbf{g}\mathbf{v})-\boldsymbol{\nabla}\hat{P}-\nabla\hat{\boldsymbol{\Pi}}+\sum_{\alpha} n^{\alpha}\overline{\mathbf{F}}^{\alpha},
\end{aligned} \tag{6}$$

$$\begin{aligned}
\partial_t\hat{\epsilon} &= -\boldsymbol{\nabla}\cdot(\mathbf{v}\hat{\epsilon})-\hat{P}\boldsymbol{\nabla}\cdot\mathbf{v}-\hat{\boldsymbol{\Pi}}:\boldsymbol{\nabla}\mathbf{v}\\
&\quad +\nabla\left(\sum_{\alpha} S^{\alpha}\hat{T}^2\nabla\left(\frac{\hat{\mu}^{\alpha}}{\hat{T}}\right)\right)-\nabla\left(\hat{\kappa}\hat{T}^2\nabla\left(\frac{1}{\hat{T}}\right)\right)\\
&\quad -\sum_{\alpha\beta}\left[\hat{T}\nabla\left(\frac{\hat{\mu}^{\alpha}}{\hat{T}}\right)-\overline{\mathbf{F}}^{\alpha}\right]D^{\alpha\beta}\overline{\mathbf{F}}^{\beta}-\nabla\left(\sum_{\alpha} S^{\alpha}\overline{\mathbf{F}}^{\alpha}\hat{T}\right)\\
&\quad -\sum_{\alpha} S^{\alpha}\overline{\mathbf{F}}^{\alpha}\nabla\hat{T}.
\end{aligned}$$

These equations have been derived from the microscopic dynamics in Sec. IV. The quantities appearing in these equations are enumerated and defined in what follows. The temperature $\hat{T}$, chemical potential $\hat{\mu}^{\alpha}$ of species α, and pressure $\hat{P}$ are defined in the usual way[18] from the entropy density $\hat{s}$ introduced after Eq. (5), which is

$$\frac{1}{\hat{T}}=\frac{\partial}{\partial\hat{\epsilon}}\hat{s}(n^A,n^B,\hat{\epsilon}),\quad \frac{\hat{\mu}^A}{\hat{T}}=-\frac{\partial}{\partial n^A}\hat{s}(n^A,n^B,\hat{\epsilon}),$$

$$\frac{\hat{\mu}^B}{\hat{T}} = -\frac{\partial}{\partial n^B}\hat{s}(n^A, n^B, \hat{\epsilon}), \tag{7}$$

$$\hat{P} = \hat{T}\hat{s} - \hat{\epsilon} + \sum_\alpha n^\alpha \mu^\alpha.$$

These intensive quantities become field quantities in Eq. (6) when evaluated at the local values of $n^\alpha_{\mathbf{r}}, \hat{\epsilon}_{\mathbf{r}}$. It is quite remarkable that the equations of state appearing in the hydrodynamic equations (6) are those of the hard-core system. This is a direct consequence of the functional form of the entropy functional in Eq. (5).

The viscous stress tensor in Eq. (6) has a usual form[8]

$$\hat{\mathbf{\Pi}} = -\hat{\eta}[\nabla\mathbf{v} + \nabla\mathbf{v}^T - \tfrac{2}{3}\nabla\cdot\mathbf{v}\mathbf{1}] - \hat{\zeta}\nabla\cdot\mathbf{v}\mathbf{1}. \tag{8}$$

The shear and bulk viscosities $\hat{\eta}$ and $\hat{\zeta}$ are defined through the usual Green–Kubo expressions in Eqs. (156) in Sec. IV. The rest of transport coefficients $D^{\alpha\beta}$, S^α, and $\hat{\kappa}$ in Eqs. (6) are related to mass diffusion, cross effects, and heat conductivity, respectively. Again, we have in Eqs. (144), (151), and (161) in Sec. IV their expression in terms of Green–Kubo formulas.[6,19,20] Not all the transport coefficients are independent, because momentum conservation implies the following conditions [see Eqs. (145) and (152) in Sec. IV]:

$$\sum_\alpha m_\alpha D^{\alpha\beta}_{\mathbf{r}} = 0, \quad \sum_\alpha m_\alpha S^\alpha_{\mathbf{r}} = 0. \tag{9}$$

The remaining quantity appearing in Eqs. (6) is the long-range force $\overline{\mathbf{F}}^\alpha_{\mathbf{r}}$, which is defined by

$$\overline{\mathbf{F}}^\alpha_{\mathbf{r}} = \sum_\beta \int d\mathbf{r}'\ \overline{\mathbf{F}}^{\alpha\beta}_{\mathbf{r}\mathbf{r}'} n^\beta_{\mathbf{r}'} \tag{10}$$

and $\overline{\mathbf{F}}^{\alpha\beta}_{\mathbf{r}\mathbf{r}'}$ is the long-range attractive force that a molecule of specie β at $\mathbf{r}'$ exerts on a molecule of specie α at $\mathbf{r}$. We can write this force in terms of the functional derivatives with respect to the density field of the total long-range potential energy $\overline{\Phi}$ defined in Eq. (4) as

$$\overline{\mathbf{F}}^\alpha_{\mathbf{r}} = -\boldsymbol{\nabla}\frac{\delta\overline{\Phi}}{\delta n^\alpha_{\mathbf{r}}}. \tag{11}$$

By neglecting in Eq. (6) the terms containing the long-range force $\overline{\mathbf{F}}^\alpha_{\mathbf{r}}$, we recover the equations for the diffusion of heat and mass of a mixture of hard-core fluids.[6–8] We have made plausible in Sec. IV that, under the van der Waals assumptions, *all the transport coefficients correspond to those of a purely hard-core system*. Therefore, Eqs. (6) are a generalization of the above-mentioned equations whenever the potential of interaction can be decomposed, according to van der Waals, in terms of a hard-core and a long-range attractive tail. It is quite remarkable that the van der Waals approximation (1) for the intermolecular potential has a direct but nontrivial reflection in the hydrodynamic equations, where all the effects of the long-range part of the potential are ''superimposed'' on the usual hydrodynamics of the hard-core fluid. Note that when only one species is present, Eqs. (9) imply that the diffusion and cross-effect coefficients vanish. In this particular case, Eqs. (6) reduce to the hydrodynamic equations presented in Ref. 16 for a van der Waals simple fluid.

The simplest possible model for a hard-core fluid mixture is the excluded volume model of van der Waals, which does not display phase separation.[21] The presence of the long-range attractive tail of the potential is the responsible for the phase separation, either at equilibrium or in dynamic situations governed by Eqs. (6). As will be apparent in Sec. II B, the long-range force can be decomposed in two parts. One of them is purely local and gives rise to typical van der Waals attractive terms in the thermodynamic pressure and chemical potentials. The other is nonlocal and is the responsible for the surface tension appearing at the interfaces that form when the mixture phase separate.

A. General properties

The set of equations (6) have the GENERIC structure, as shown in Sec. IV. For this reason, they automatically satisfy that the total energy (2) is exactly conserved and that the time derivative of the total entropy (5) is positive (positive entropy production). It can also be shown that the reversible part of Eqs. (6), which is obtained by setting the transport coefficients to zero, produces no entropy. All these properties can be explicitly checked by direct calculation of the time derivatives of Eqs. (2) and (5). In order to pursue this check, we should recall that the transport coefficients satisfy the conditions $D^{\alpha\alpha} > 0$, $\hat{\kappa} > 0$, and $D^{\alpha\alpha}\hat{\kappa} > \hat{T}S^{\alpha 2}$, as shown in Sec. V. Equations (6) also conserve the total momentum defined as

$$\mathbf{P} = \int d\mathbf{r}\ \mathbf{g}_{\mathbf{r}}. \tag{12}$$

By taking the time derivative of $\mathbf{P}$ and using the momentum equation in Eqs. (6), we easily arrive at

$$\dot{\mathbf{P}} = \sum_{\alpha\beta} \int d\mathbf{r}\ d\mathbf{r}'\ n^\alpha_{\mathbf{r}} n^\beta_{\mathbf{r}'} \overline{\mathbf{F}}^{\alpha\beta}_{\mathbf{r}\mathbf{r}'}, \tag{13}$$

where we have neglected those terms that are the integral of a divergence, which can be converted to surface integrals. However, the remaining term is also zero because the long-range force satisfies Newton's third law $\overline{\mathbf{F}}^{\alpha\beta}_{\mathbf{r}\mathbf{r}'} = -\overline{\mathbf{F}}^{\beta\alpha}_{\mathbf{r}'\mathbf{r}}$ and, therefore, $\dot{\mathbf{P}} = 0$. Finally, the total mass of each species,

$$M^\alpha = \int d\mathbf{r}\ m_\alpha n^\alpha_{\mathbf{r}}, \tag{14}$$

is also a conserved quantity, as can be easily seen by computing its time derivative, using the density equations (6) together with properties (9).

Because $\dot{S}[x] \geqslant 0$, the state x of the fluid mixture will evolve according to Eqs. (6) towards higher values of the entropy functional but conserving the values of the energy, mass, and momentum. The final equilibrium state of Eqs. (6) can be obtained then by maximizing the entropy functional in Eq. (5) subjected to the restrictions of conservation of mass, momentum, and energy. That is, we maximize the functional

$$S[x]+\beta E[x]+\sum_\alpha \beta\lambda^\alpha N_\alpha[x]-\beta\mathbf{V}\cdot\mathbf{P}[x], \tag{15}$$

where β, λ^α and $\mathbf{V}$ are Lagrange multipliers. The result of the unrestricted maximization of Eq. (15) is simply

$$-\frac{\hat{\mu}^\alpha}{\hat{T}_\mathbf{r}}+\beta m_\alpha\frac{\mathbf{v}_\mathbf{r}^2}{2}+\beta\frac{\delta\Phi}{\delta n_\mathbf{r}^\alpha}+\beta\lambda^\alpha=0,$$

$$\frac{\mathbf{g}_\mathbf{r}}{\rho_\mathbf{r}}-\mathbf{V}=0, \tag{16}$$

$$\frac{1}{\hat{T}_\mathbf{r}}-\beta=0.$$

In other words, the temperature field is constant at equilibrium, the velocity field is also constant (and we can choose without loosing generality $\mathbf{V}=0$), and the chemical potential satisfies the following equation:

$$\hat{\mu}_\mathbf{r}^\alpha-\frac{\delta\Phi}{\delta n_\mathbf{r}^\alpha}=\lambda^\alpha. \tag{17}$$

B. Local approximation

Our claim is that Eqs. (6) describe the dynamics of a fluid mixture that can phase separate according to the van der Waals equation of state. This might not be obvious despite of the fact that the fundamental assumption (1) implicit in the van der Waals picture has been taken. In order to prove this statement and to make contact with gradient theories for phase separating fluids,[1] we study a local approximation for the long-range forces $\overline{\mathbf{F}}_\mathbf{r}^\alpha$ that appear in the hydrodynamic equations (6). If the space variations of the density field are small in the range of the attractive mean-field potential, then we are allowed to perform the following local approximation.[1] From Eq. (4) it is easily shown that

$$\overline{\Phi}=-\frac{1}{2}\sum_{\alpha\beta}\int d\mathbf{r}\; n_\mathbf{r}^\alpha n_\mathbf{r}^\beta a_{\alpha\beta}-\frac{1}{4}\sum_{\alpha\beta}\int d\mathbf{r}\int d\mathbf{r}'[n_\mathbf{r}^\alpha-n_{\mathbf{r}'}^\alpha]\times[n_\mathbf{r}^\beta-n_{\mathbf{r}'}^\beta]\overline{\phi}_{\mathbf{r}\mathbf{r}'}^{\alpha\beta}, \tag{18}$$

where

$$a_{\alpha\beta}=-\int d\mathbf{s}\;\overline{\phi}^{\alpha\beta}(\mathbf{s})\geqslant 0. \tag{19}$$

Under the assumption of slowly varying density fields, the last term in Eq. (18) can be Taylor expanded with the result

$$\overline{\Phi}=-\frac{1}{2}\sum_{\alpha\beta}a_{\alpha\beta}\int d\mathbf{r}\; n_\mathbf{r}^\alpha n_\mathbf{r}^\beta+\frac{1}{2}\sum_{\alpha\beta}c_{\alpha\beta}\int d\mathbf{r}\;\nabla n_\mathbf{r}^\alpha\cdot\nabla n_\mathbf{r}^\beta, \tag{20}$$

where

$$c_{\alpha\beta}=-\frac{1}{6}\int d\mathbf{s}\; s^2\overline{\phi}^{\alpha\beta}(\mathbf{s})\geqslant 0. \tag{21}$$

The first interesting consequence of this local approximation is obtained after substituting Eq. (20) into the equilibrium condition (17):

$$\hat{\mu}_\mathbf{r}^\alpha+\sum_\beta a_{\alpha\beta}n_\mathbf{r}^\alpha+\sum_\beta c_{\alpha\beta}\nabla^2 n_\mathbf{r}^\alpha=\lambda^\alpha. \tag{22}$$

We recognize in the term $\hat{\mu}_\mathbf{r}^\alpha+\Sigma_\beta a_{\alpha\beta}n_\mathbf{r}^\alpha$ the van der Waals expression for the chemical potential[1] and, therefore, the above equilibrium condition predicts the usual phase separation of a van der Waals mixture.

It is also illustrative to consider the momentum equation in Eqs. (6) within this local approximation. The force $\overline{\mathbf{F}}_\mathbf{r}^\alpha$ can be computed from Eqs. (11) and (20) and one obtains

$$\overline{\mathbf{F}}_\mathbf{r}^\alpha=\nabla\left(\sum_\beta a_{\alpha\beta}n_\mathbf{r}^\beta\right)+\sum_\beta c_{\alpha\beta}\nabla\nabla^2 n_\mathbf{r}^\beta. \tag{23}$$

The effect of the long-range force in the momentum equation in Eqs. (6) can be obtained by computing the term $\Sigma_\alpha n_\mathbf{r}^\alpha\overline{\mathbf{F}}_\mathbf{r}^\alpha$ as

$$\sum_\alpha n_\mathbf{r}^\alpha\overline{\mathbf{F}}_\mathbf{r}^\alpha=\nabla\left(\frac{1}{2}\sum_{\alpha\beta}a_{\alpha\beta}n_\mathbf{r}^\alpha n_\mathbf{r}^\beta\right)+\sum_{\alpha\beta}c_{\alpha\beta}n_\mathbf{r}^\alpha\nabla\nabla^2 n_\mathbf{r}^\beta=-\nabla\left(-\frac{1}{2}\sum_{\alpha\beta}a_{\alpha\beta}n_\mathbf{r}^\alpha n_\mathbf{r}^\beta+\mathbf{P}_\mathbf{r}\right), \tag{24}$$

where the surface stress tensor $\mathbf{P}_\mathbf{r}$ is given by[1]

$$\mathbf{P}_\mathbf{r}^{\mu\nu}=\sum_{\alpha\beta}2c_{\alpha\beta}\left[\frac{1}{6}\nabla^\mu n_\mathbf{r}^\alpha\nabla^\nu n_\mathbf{r}^\beta+\frac{1}{12}(\nabla n_\mathbf{r}^\alpha\cdot\nabla n_\mathbf{r}^\beta)\delta^{\mu\nu}-\frac{1}{3}n_\mathbf{r}^\alpha\nabla^\mu\nabla^\nu n_\mathbf{r}^\beta-\frac{1}{6}n_\mathbf{r}^\alpha\nabla^2 n_\mathbf{r}^\beta\delta^{\mu\nu}\right]. \tag{25}$$

In this way, the momentum equation becomes

$$\partial_t\mathbf{g}_\mathbf{r}=-\nabla\cdot(\mathbf{g}_\mathbf{r}\mathbf{v}_\mathbf{r})-\nabla\left(\hat{P}_\mathbf{r}-\frac{1}{2}\sum_{\alpha\beta}a_{\alpha\beta}n_\mathbf{r}^\alpha n_\mathbf{r}^\beta\right)-\nabla\mathbf{P}_\mathbf{r}-\nabla\hat{\mathbf{\Pi}}_\mathbf{r}. \tag{26}$$

We recognize in the combination $(\hat{P}_\mathbf{r}-\frac{1}{2}\Sigma_{\alpha\beta}a_{\alpha\beta}n_\mathbf{r}^\alpha n_\mathbf{r}^\beta)$ the van der Waals pressure of a fluid mixture,[1] whereas the capillary stress tensor $\mathbf{P}_\mathbf{r}$ in Eq. (26) is used thoroughly in the study of equilibrium interfacial phenomena and it is directly related to surface tension.[1] The dynamic equation (26) is, therefore, the nonequilibrium generalization of the condition of mechanical equilibrium in the usual gradient theory for equilibrium interfaces. Note that one of the implicit assumptions in the hydrodynamic equations (6) is that of local equilibrium. The local equilibrium assumption valid not only for the bulk but also for the interfacial regions of a phase-separated fluid has been validated from molecular dynamics simulations for a one component fluid[22] and it is expected that a similar situation occurs for multicomponent fluids.

C. Binary mixture case

It proves convenient to restrict to a binary fluid and to perform a change of variables from $\{n^A,n^B,\mathbf{g},\hat{\boldsymbol{\epsilon}}\}$ to $\{\rho,c,\mathbf{g},u\}$, with the latter variables defined as

$$\rho = m_A n^A + m_B n^B,$$
$$c = \frac{m_A n^A}{m_A n^A + m_B n^B}, \tag{27}$$
$$u = \hat{\epsilon} - \frac{1}{2}\sum_{\alpha\beta} a_{\alpha\beta} n^\alpha n^\beta.$$

These variables are the total mass density ρ, the mass fraction c of component A, and the full local internal energy u. This last quantity has a clear microscopic interpretation as the internal energy density of those molecules in a small region of space that are interacting with the *full* potential $\phi = \hat{\phi} + \overline{\phi}$, where the long-range contribution is treated in mean field, given that the range of $\overline{\phi}$ is much larger than the size of the region being considered.

The relationships inverse to those in Eq. (27) are

$$n^A = \frac{\rho c}{m_A}, \quad n^B = \frac{\rho(1-c)}{m_B},$$
$$\hat{\epsilon} = u + \overline{u}(\rho, c), \tag{28}$$
$$\overline{u}(\rho,c) = \frac{\rho^2}{2}\left[\frac{a_{AA}}{m_A^2}c^2 + 2\frac{a_{AB}}{m_A m_B}c(1-c) + \frac{a_{BB}}{m_B^2}(1-c)^2\right].$$

We introduce the specific entropy s^{vdw} (entropy per unit mass) as a function of the new variables:

$$s^{\mathrm{vdW}}(\rho,c,u) = \frac{1}{\rho}\hat{s}(n^A, n^B, \hat{\epsilon}) = \frac{1}{\rho}\hat{s}\left(\frac{\rho c}{m_A}, \frac{\rho(1-c)}{m_B}, u + \overline{u}\right). \tag{29}$$

We emphasize that the above entropy is actually the specific entropy of the van der Waals model of a binary mixture, expressed in the variables ρ, c, u.

In what follows, we will need the derivatives of the specific entropy. We introduce the temperature of the van der Waals model as

$$\frac{1}{T^{\mathrm{vdW}}} = \frac{\partial \rho s^{\mathrm{vdW}}}{\partial u} \tag{30}$$

and easily obtain from Eq. (29) the functional form of T^{vdW}:

$$T^{\mathrm{vdW}}(\rho,c,u) = \hat{T}\left(\frac{\rho c}{m_A}, \frac{\rho(1-c)}{m_B}, u + \overline{u}\right); \tag{31}$$

that is, the temperature of the van der Waals fluid mixture is given by the temperature of the hard-core fluid mixture, evaluated at the variables ρ, c, u. In a similar way, we introduce the chemical potential per unit mass μ_c^{vdW} as

$$\frac{\partial s^{\mathrm{vdW}}}{\partial c} = -\frac{\mu_c^{\mathrm{vdW}}}{T^{\mathrm{vdW}}}. \tag{32}$$

By using Eq. (29) we easily arrive at

$$\mu_c^{\mathrm{vdW}} = \frac{\hat{\mu}^A}{m_A} - \frac{\hat{\mu}^B}{m_B} - \rho[\alpha_1 c + \alpha_2], \tag{33}$$

where we have introduced the following interaction parameters:

$$\alpha_1 = \frac{a_{AA}}{m_A m_A} + \frac{a_{BB}}{m_B m_B} - 2\frac{a_{AB}}{m_A m_B},$$
$$\alpha_2 = \frac{a_{AB}}{m_A m_B} - \frac{a_{BB}}{m_B m_B}. \tag{34}$$

By using the dynamic equations for n^A, n^B we can easily obtain the corresponding dynamic equations for ρ, c, which are

$$\partial_t \rho = -\nabla \rho \mathbf{v},$$
$$\partial_t c = -\mathbf{v}\cdot\nabla c + \frac{1}{\rho}\nabla\left(D\hat{T}\nabla\frac{1}{\hat{T}}\left(\frac{\hat{\mu}^A}{m_A} - \frac{\hat{\mu}^B}{m_B}\right)\right) + \frac{1}{\rho}\nabla D\left(\frac{\overline{\mathbf{F}}^B}{m_B} - \frac{\overline{\mathbf{F}}^A}{m_A}\right) + \frac{1}{\rho}\nabla(S\nabla\hat{T}), \tag{35}$$

where we have introduced the coefficients $S = S^A m_A = -S^B m_B$ and $D = m_A^2 D^{AA} = -m_B m_A D^{AB} = m_B^2 D^{BB}$. These equalities derive from Eqs. (152) and (145).[6]

By using the local approximation (23) for the long-range forces and after some algebra, one arrives at

$$\rho\frac{d}{dt}c = \nabla(D\nabla(\mu_c^{\mathrm{vdW}} + \nabla^2((\gamma_1 c + \gamma_2)\rho))) + \nabla\left(\left(S - \frac{D}{T^{\mathrm{vdW}}}[\mu_c^{\mathrm{vdW}} + (\alpha_1 c + \alpha_2)\rho]\right)\nabla T^{\mathrm{vdW}}\right), \tag{36}$$

where we have introduced the usual substantial derivative $d/dt = \partial_t + \mathbf{v}\cdot\nabla$ and the following interaction parameters:

$$\gamma_1 = \frac{c_{AA}}{m_A m_A} + \frac{c_{BB}}{m_B m_B} - 2\frac{c_{AB}}{m_A m_B},$$
$$\gamma_2 = \frac{c_{AB}}{m_A m_B} - \frac{c_{BB}}{m_B m_B}. \tag{37}$$

We observe that the dynamic equations for the new variables ρ, c are the continuity equation for the total mass density ρ and an advection-diffusion equation, Eq. (36), for the mass fraction c. For a quiescent isothermal incompressible ($\dot{\rho} = 0$) fluid, it becomes the well-known Cahn–Hilliard equation.[23,24] Therefore, the above equation is the appropriate generalization for a nonequilibrium van der Waals mixture, and the previous derivation can be understood as a microscopic basis for the nonequilibrium Cahn–Hilliard equation. The nontrivial form in which thermal gradients affect the evolution of the mass fraction is quite remarkable. Even if the Soret-like coefficient S can be neglected, it is not correct to neglect cross effects (gradients of temperature inducing flux of mass), as important contributions due to the diffusionlike coefficient D still exist. Finally, we could write the hydrodynamic equation for the internal energy u, in order to have a closed set of equations for ρ, c, u, but nothing essential is gained in doing so.

In the local approximation, the energy functional in Eq. (2) becomes a local functional of the density fields, hard-core internal energy, and also of the gradients of the density fields.

It is apparent that such gradient terms do not occur in the entropy functional in Eq. (5) within the van der Waals picture. Of course, if instead of using the hard-core internal energy variable $\hat{\epsilon}$ we make a change of variable and use a total internal energy variable defined as

$$e_{\mathbf{r}} = \hat{\epsilon}_{\mathbf{r}} - \frac{1}{2}\sum_{\alpha\beta} a_{\alpha\beta} n_{\mathbf{r}}^{\alpha} n_{\mathbf{r}}^{\beta} + \frac{1}{2}\sum_{\alpha\beta} c_{\alpha\beta} \boldsymbol{\nabla} n_{\mathbf{r}}^{\alpha} \cdot \boldsymbol{\nabla} n_{\mathbf{r}}^{\beta}, \tag{38}$$

then the energy functional does not depend on the gradients of the density field and the entropy does depend on these gradients. We believe that one of the benefits of the microscopic derivation presented in this paper is the fact that a well-defined meaning is ascribed to the energy density variable. For example, in phenomenological theories based on linear irreversible thermodynamics, it is postulated a dependence of the entropy density on the gradients of the density fields.[11] From the presentation in this paper, it is apparent that this is possible only if the energy density field is given by Eq. (38). In a phenomenological approach it is not evident at all which is the physical meaning to be associated to the energy density field, i.e., $\hat{\epsilon}_{\mathbf{r}}, \epsilon_{\mathbf{r}}$ or $u_{\mathbf{r}}$, despite the fact that very different forms of the hydrodynamic equations are obtained in each case.

A general remark can be made about the local approximation. The basic assumption behind this local approximation, which is that the density fields do not change much within the range of the long-range potential, is expected to be valid near critical points, where the density profiles are usually very broad. In subcritical regions well below the critical points we expect that the density fields vary on the same length scale as the long-range potential and renders the local approximation dubious. In this case, it seems more appropriate to use the nonlocal form (6) for the hydrodynamic equations. Actually, it may appear as an advantage from a practical computational point of view to use these nonlocal equations. In fact, the local equations involve high-order spatial derivatives (third order in the momentum equation and fourth order in the density equations) that must be resolved accurately at interfacial regions. Clearly, an integral representation of surface effects may be much more stable than high-order derivatives.

The hydrodynamic model presented in this paper belongs to the class of phase fields models for phase-separating fluids.[10] The main difference to many existing phase field models is that the phase fields here are not mathematical devices used to pinpoint interfacial regions, but have actually a definite physical meaning as they are the number density fields of the mixture.[12] The spirit of the model presented, though, is similar to phase field models in which interfaces appear whenever the system is in a region of thermodynamic parameters where phase separation occurs. In this case, regions of different concentrations of components appear and they are separated by transition regions or diffuse interfaces. It is noteworthy that there is no need in this sort of theories to apply boundary conditions on the interfaces separating two phases. The boundaries appear (or disappear) as a dynamical process. Critical and subcritical states are treated on an equal footing and there is no need to worry about topological changes of the interfaces, a subtle problem in interface tracking algorithms. This makes the model presented in this paper very suitable for numerical simulations of nonequilibrium phase separation in mixtures.

The remainder of the paper deals with the actual derivation of Eqs. (6) from the underlying microscopic dynamics at a molecular level.

III. GENERIC FRAMEWORK

In this section, we briefly summarize the GENERIC framework.[14] In particular, we present the microscopic definitions of the building blocks of the GENERIC framework.[13,15] For a recent review of this background, see Ref. 25. In the next section we will compute explicitly these blocks for the particular case of a fluid mixture.

A. Microscopic dynamics

We denote the collection of coordinates and momenta of each molecule by z and the Hamiltonian by $H(z)$. Hamilton's equations can be written in a compact form as

$$\dot{z} = L_0 \frac{\partial H(z)}{\partial z}, \tag{39}$$

where the antisymmetric matrix L_0 has the form of a block diagonal matrix with the blocks given by

$$\begin{pmatrix} 0 & \mathbf{1} \\ -\mathbf{1} & 0 \end{pmatrix}, \tag{40}$$

where $\mathbf{1}$ is the unit tensor. The time derivative of any function $X(z)$ of phase space is given by

$$\dot{X}(z) = \frac{\partial X}{\partial z} L_0 \frac{\partial H}{\partial z} = iLX(z), \tag{41}$$

where we have introduced the Liouville operator iL. The Liouville equation that governs the probability density $\rho(z,t)$ in the microscopic phase space is given by

$$\partial_t \rho(z,t) = -iL\rho(z,t). \tag{42}$$

Any distribution function that depends on z through the dynamical invariants $I(z)$ of the system is an equilibrium solution of the Liouville equation (42). For the case that the actual values I_0 of the dynamical invariants are known with precision, the equilibrium ensemble is given by

$$\rho^{\mathrm{eq}}(z) = \frac{1}{\Omega_0}\delta(I(z) - I_0), \tag{43}$$

where Ω_0 is the normalization factor. When there are no other dynamical invariant apart from the total energy, the above ensemble is the microcanonical ensemble.

B. Mesoscopic dynamics

At a coarse-grained level of description, the system is described by a set of functions $X_k(z)$ which depend on the set of position and momenta z of the molecules of the system. The selection of the relevant variables $X_k(z)$ is a crucial step in the description of a nonequilibrium system. One basic requirement on the set of relevant variables is that they should provide for a *closed* description of the system. This will be possible in general only if the relevant variables are

all those functions that evolve in a time scale much larger than the time scale of evolution of the microstates z. We will discuss in Sec. IV A the relevant hydrodynamic variables for a fluid mixture.

When a clear separation of time scales exists, Green[26] and later Zwanzig[27] derived from the microscopic dynamics of the system a general Fokker–Planck equation for the set of relevant variables x:

$$\partial_t P(x,t) = -\frac{\partial}{\partial x}\left[A(x) + M(x)\frac{\partial S}{\partial x}\right]P(x,t) + k_B \frac{\partial}{\partial x} M(x) \frac{\partial}{\partial x} P(x,t). \tag{44}$$

The different objects in this equation have a well-defined microscopic definition. For example,

$$A(x) = \langle iLX \rangle^x, \tag{45}$$

where the constrained average is defined by

$$\langle \cdots \rangle^x = \frac{1}{\Omega(x)} \int dz\ \delta(X(z) - x) \cdots, \tag{46}$$

where $\delta(X(z)-x)$ actually stands for a product of Dirac delta functions, one for every function $X_k(z)$. The "volume" of phase space compatible with a prescribed value x of the relevant variables is

$$\Omega(x) = \int dz\ \delta(X(z) - x) \tag{47}$$

and is closely related to the entropy of the mesolevel x which is defined through

$$S(x) \equiv k_B \ln \Omega(x), \tag{48}$$

where k_B is Boltzmann's constant.

Finally, the irreversible symmetric operator M is the matrix of transport coefficients expressed in the form of Green–Kubo formulas,

$$M(x) = \frac{1}{2k_B} \int_{-\infty}^{\infty} \langle \delta iLX \exp\{iQLt'\} \delta iLX \rangle^x\ dt', \tag{49}$$

where $\delta iLX = iLX - \langle iLX \rangle^x$ is the so-called projected current. The dynamic operator $\exp\{iQLt'\}$ is usually named the projected dynamics, which is, strictly speaking, different from the real dynamics $\exp\{iLt'\}$. The projection operator Q is defined from its action on any phase function $F(z)$ (Ref. 27):

$$QF(z) = F(z) - \langle F \rangle^{X(z)}. \tag{50}$$

The projected dynamics can be usually approximated by the real dynamics, but then the upper infinite limit of integration in Eq. (49) has to be replaced by τ, a time which is long in front of the correlation time of the integrand, but short in front of the time scale of evolution of the macroscopic variables. This is the well-known plateau problem.[28,29] The operator M is symmetric and positive definite.[29]

It may happen that the set of relevant variables $X(z)$ has the important property that the microscopic Hamiltonian can be written as a function of the relevant variables, that is,

$$H(z) = E(X(z)), \tag{51}$$

where $E(x)$ is a function that defines the energy at the mesoscopic level. When this property (51) is satisfied, then the reversible drift (45) of the dynamics can be written as[13]

$$A(x) = L(x)\frac{\partial E}{\partial x}, \tag{52}$$

where the reversible antisymmetric operator L is defined by

$$L(x) = \left\langle \frac{\partial X}{\partial z} L_0 \frac{\partial X}{\partial z} \right\rangle^x. \tag{53}$$

The Fokker–Planck equation takes then the GENERIC form[14]

$$\partial_t P(x,t) = -\frac{\partial}{\partial x}\left[L(x)\frac{\partial E}{\partial x} + M(x)\frac{\partial S}{\partial x}\right]P(x,t) + k_B \frac{\partial}{\partial x} M(x) \frac{\partial}{\partial x} P(x,t). \tag{54}$$

The stochastic differential equation that is mathematically equivalent to the above Fokker–Planck equation is given by

$$dx = \left[L(x)\frac{\partial E}{\partial x} + M(x)\frac{\partial S}{\partial x} + k_B \frac{\partial}{\partial x} M(x)\right]dt + d\tilde{x}, \tag{55}$$

where $d\tilde{x}$ is a linear combination of independent increments of the Wiener process that satisfy a fluctuation–dissipation theorem in the form $d\tilde{x}\ d\tilde{x} = 2k_B M(x) dt$. In situations where the thermal fluctuations can be neglected [formally in the limit $k_B \to 0$ (Ref. 29)], one obtains a set of deterministic equations of the form

$$\dot{x} = L(x)\frac{\partial E}{\partial x} + M(x)\frac{\partial S}{\partial x}. \tag{56}$$

As discussed in Ref. 14, the advantage of writing the Fokker–Planck equation in the GENERIC form (54) is that the matrices L, M satisfy the following degeneracy properties:

$$L \cdot \frac{\partial S}{\partial x} = 0, \quad M \cdot \frac{\partial E}{\partial x} = 0. \tag{57}$$

These cross properties, together with the symmetry properties, reduce the possible forms of the operators L, M and may help in the phenomenological formulation of new models for complex systems.

C. Equilibrium at the coarse-grained level

The equilibrium probability density at the coarse-grained level is given by

$$P(x) = \int dz\ \delta(X(z) - x) \rho^{\mathrm{eq}}(z), \tag{58}$$

where $\rho^{\mathrm{eq}}(z)$ is the equilibrium ensemble. This is the well-known rule for relating the probability density of a random variable with the probability density of a function of the random variable.

If the dynamical invariants can be written as a function of the relevant variables, that is, $I(z)=\mathcal{I}(X(z))$, and the microscopic ensemble is given by Eq. (43), and then the probability in Eq. (58) takes the form

$$P(x)=\frac{1}{\Omega_0}\delta(\mathcal{I}(x)-I_0)\exp\{S(x)/k_B\}. \tag{59}$$

This expression is a generalization of Einstein's formula for equilibrium fluctuations for the case that there exist dynamical invariants in the system which can be written in terms of the relevant variables.[30] In the next section, following the methodology presented in Ref. 16, we will compute the entropy function for a fluid mixture by first computing $P(x)$ through Eq. (58) and then identifying $S(x)$ from Eq. (59).

IV. MICROSCOPIC CALCULATION OF THE GENERIC BUILDING BLOCKS

A. Relevant variables for a fluid mixture

At the most microscopic level, a fluid mixture is described by $z=\{\mathbf{q}_{i_\alpha},\mathbf{p}_{i_\alpha}\}$, where $\mathbf{q}_{i_\alpha}$ is the position of particle i_α of species α and $\mathbf{p}_{i_\alpha}$ is the momentum of particle i_α of species $\alpha=1,\ldots,r$. The Hamiltonian of the system is

$$H(z)=\sum_{\alpha}^{r}\sum_{i_\alpha}^{N^\alpha}\frac{\mathbf{p}_{i_\alpha}^2}{2m_\alpha}+\frac{1}{2}\sum_{\alpha\beta}^{r}\sum_{i_\alpha j_\beta}^{N^\alpha N^\beta}\phi_{i_\alpha j_\beta}. \tag{60}$$

Here, m_α is the mass of the molecules of specie α, and $\phi_{i_\alpha j_\beta}$ is the potential energy of interaction between molecule i_α of species α and molecule j_β of species β. This potential energy depends only on the relative positions of both molecules. Note that the index i_α runs from 1 to N^α, which is the total number of particles of specie α. We will assume that the potential can be decomposed according to Eq. (1).

The hydrodynamic fields for which a reasonable hydrodynamic description is valid can only be defined in terms of spatially discrete variables (or smooth fields that have a finite number of Fourier components). In order to define the set of discrete hydrodynamic relevant variables, we first need to perform a partition of physical space into a set of M nonoverlapping cells. For every cell labeled μ in which the space is divided one has a characteristic function $\chi_\mu(\mathbf{r})$, which takes the value 1 if the point $\mathbf{r}$ belongs to the cell μ and zero otherwise. The characteristic function satisfies the partition of unity property

$$\sum_{\mu}\chi_\mu(\mathbf{r})=1. \tag{61}$$

The state of the system at the mesoscopic level of description will be given by the numerical values $x=\{N_\mu^\alpha,\mathbf{P}_\mu,\hat{\mathcal{E}}_\mu\}$, which take the following discrete hydrodynamic variables:

$$N_\mu^\alpha(z)=\sum_{i_\alpha}^{N^\alpha}\chi_\mu(\mathbf{q}_{i_\alpha}),$$

$$\mathbf{P}_\mu(z)=\sum_{\alpha}^{r}\sum_{i_\alpha}^{N^\alpha}\mathbf{p}_{i_\alpha}\chi_\mu(\mathbf{q}_{i_\alpha}), \tag{62}$$

$$\hat{\mathcal{E}}_\mu(z)=\sum_{\alpha}^{r}\sum_{i_\alpha}^{N^\alpha}\hat{\epsilon}_{i_\alpha}\chi_\mu(\mathbf{q}_{i_\alpha}).$$

We have introduced

$$\hat{\epsilon}_{i_\alpha}=\frac{m_\alpha}{2}\left(\frac{\mathbf{p}_{i_\alpha}}{m_\alpha}-\mathbf{v}_\mu(z)\right)^2+\hat{\phi}_{i_\alpha}, \tag{63}$$

where the potential energy associated to molecule i_α due to its *hard-core* interaction with any other molecule of the system is given by

$$\hat{\phi}_{i_\alpha}=\frac{1}{2}\sum_{\beta}^{r}\sum_{j_\beta}^{N^\beta}\hat{\phi}_{i_\alpha j_\beta}. \tag{64}$$

The phase function $N_\mu^\alpha(z)$ in Eqs. (62) is simply the number of molecules of species α that happen to be in cell μ when the microstate is z. It is apparent from Eq. (61) that $\Sigma_\mu N_\mu^\alpha(z)=N^\alpha$; that is, the total number of molecules of specie α is constant, irrespective of the microstate z. In a similar way, $\mathbf{P}_\mu$ is the momentum of all the molecules that are in cell μ. The velocity $\mathbf{v}_\mu$ of the center of mass of the molecules in cell μ is defined by

$$\mathbf{v}_\mu(z)=\frac{\mathbf{P}_\mu(z)}{M_\mu(z)}, \tag{65}$$

where $M_\mu=\Sigma_\alpha m_\alpha N_\mu^\alpha(z)$ is the total mass of cell μ. Finally, $\hat{\mathcal{E}}_\mu$ is the internal energy of the molecules that are in cell μ. Note that the internal energy does not contain the long-range part of the potential. We call this internal energy the *hard-core internal energy*.

It is straightforward to show by using the definitions (62) and the property (61) that the Hamiltonian (60) can be written as

$$H(z)=\sum_{\mu}\frac{\mathbf{P}_\mu^2(z)}{2M_\mu(z)}+\sum_{\mu}\hat{\mathcal{E}}_\mu(z)+\frac{1}{2}\sum_{\alpha\beta}^{r}\sum_{i_\alpha j_\beta}^{N^\alpha N^\beta}\overline{\phi}_{i_\alpha j_\beta}. \tag{66}$$

As we have mentioned in Sec. III, in order to have the GENERIC structure, it is necessary that the Hamiltonian may be expressed as a function of the relevant variables. Therefore, we need to express the last long-range potential term as a function of the relevant variables. This is possible only *if the size of the cells in which we have divided space is much smaller than the range of the attractive potential*. In this case we may insert Eq. (61) in the form

$$\sum_{\nu}\sum_{\mu}\chi_\mu(\mathbf{q}_{i_\alpha})\chi_\nu(\mathbf{q}_{j_\beta})=1, \tag{67}$$

within the sum in the long-range potential energy, that is,

$$\frac{1}{2}\sum_{\alpha\beta}^{r}\sum_{i_\alpha j_\beta}^{N^\alpha N^\beta}\overline{\phi}_{i_\alpha j_\beta}\sum_{\nu}\sum_{\mu}\chi_\mu(\mathbf{q}_{i_\alpha})\chi_\nu(\mathbf{q}_{j_\beta})$$
$$\approx\frac{1}{2}\sum_{\mu\nu}\sum_{\alpha\beta}^{r}\overline{\phi}^{\alpha\beta}(\mathbf{r}_\mu-\mathbf{r}_\nu)\sum_{i_\alpha j_\beta}^{N^\alpha N^\beta}\chi_\mu(\mathbf{q}_{i_\alpha})\chi_\nu(\mathbf{q}_{j_\beta})$$
$$=\frac{1}{2}\sum_{\mu\nu}\sum_{\alpha\beta}^{r}\overline{\phi}^{\alpha\beta}_{\mu\nu}N^\alpha_\mu(z)N^\beta_\nu(z), \tag{68}$$

where $\overline{\phi}^{\alpha\beta}_{\mu\nu}=\overline{\phi}^{\alpha\beta}(\mathbf{r}_\mu-\mathbf{r}_\nu)$. In Eq. (68) we have assumed that the long-range part of the potential can be approximated as if all the particles where located at the centers of the cells [note that $\overline{\phi}^{\alpha\beta}(r)$ is nonsingular at the origin, as all the singular behavior of the potential is assumed to be contained in $\hat{\phi}^{\alpha\beta}$]. This approximation is a good one given the small variation of $\overline{\phi}^{\alpha\beta}$ in a cell dimension. In this way, the Hamiltonian depends on the microstate z only through the relevant variables, that is,

$$H(z)=\sum_\mu\frac{\mathbf{P}^2_\mu(z)}{2M_\mu(z)}+\sum_\mu\hat{\mathcal{E}}_\mu(z)$$
$$+\frac{1}{2}\sum_{\mu\nu}\sum_{\alpha\beta}^{r}\overline{\phi}^{\alpha\beta}_{\mu\nu}N^\alpha_\mu(z)N^\beta_\nu(z). \tag{69}$$

The total momentum of the system can also be expressed in terms of the hydrodynamic relevant variables

$$\mathbf{P}(z)=\sum_\mu\mathbf{P}_\mu(z). \tag{70}$$

Because the dynamical invariants of the system are expressed in terms of the relevant variables, we have that the hydrodynamical description can be written in the GENERIC form.

In a continuum theory, one introduces the hydrodynamic *fields* rather than the discrete set of variables (62). By dividing the extensive discrete variables (62) by the volume $\mathcal{V}_\mu$ of cell μ one obtains a set of densities. We also introduce the continuum notation in which each label of the cell is denoted by the cell center position $\mathbf{r}_\mu$, and we introduce the coarse-grained Dirac's delta function

$$\overline{\delta}(\mathbf{r},\mathbf{r}_\mu)=\frac{\chi_\mu(\mathbf{r})}{\mathcal{V}_\mu}, \tag{71}$$

which has a continuum index $\mathbf{r}$ and a discrete one $\mathbf{r}_\mu$. Due to the definition of the volume of cell μ as $\mathcal{V}_\mu=\int d\mathbf{r}\chi_\mu(\mathbf{r})$, this function satisfies

$$\int d\mathbf{r}\ \overline{\delta}(\mathbf{r},\mathbf{r}_\mu)=1. \tag{72}$$

At the same time, the partition of unity (61) implies

$$\sum_\mu\mathcal{V}_\mu\overline{\delta}(\mathbf{r},\mathbf{r}_\mu)=1. \tag{73}$$

Note that in a continuum notation we understand $\Sigma_\mu\mathcal{V}_\mu$ as providing the integral $\int d\mathbf{r}$. Actually, for any arbitrary function $\overline{f}(\mathbf{r})$ whose length scale of spatial variation is much larger than the typical size of the cells, we have the approximate expressions

$$\int d\mathbf{r}\ \overline{\delta}(\mathbf{r},\mathbf{r}_\mu)\overline{f}(\mathbf{r})=\overline{f}(\mathbf{r}_\mu),$$
$$\sum_\mu\mathcal{V}_\mu\overline{f}(\mathbf{r}_\mu)\overline{\delta}(\mathbf{r},\mathbf{r}_\mu)=\overline{f}(\mathbf{r}). \tag{74}$$

The exact relationships (71) and (72) and the approximate equation (74) allow one to treat $\overline{\delta}(\mathbf{r},\mathbf{r}_\mu)$ as a truly Dirac delta function $\overline{\delta}(\mathbf{r}-\mathbf{r}_\mu)$, whenever it appears under integral signs accompanying spatially smooth functions $\overline{f}(r)$.

The *density* fields are the number density fields of each specie $n^\alpha_{\mathbf{r}}=N^\alpha_\mu/\mathcal{V}_\mu$, the momentum density field $\mathbf{g}_{\mathbf{r}}=\mathbf{P}_\mu/\mathcal{V}_\mu$, and the internal energy density fields $\hat{\boldsymbol{\epsilon}}_{\mathbf{r}}=\hat{\mathcal{E}}_\mu/\mathcal{V}_\mu$, where

$$n^\alpha_{\mathbf{r}}(z)=\sum_{i_\alpha}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha}),$$
$$\mathbf{g}_{\mathbf{r}}(z)=\sum_\alpha\sum_{i_\alpha}\mathbf{p}_{i_\alpha}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha}), \tag{75}$$
$$\hat{\boldsymbol{\epsilon}}_{\mathbf{r}}(z)=\sum_\alpha\sum_{i_\alpha}\hat{\boldsymbol{\epsilon}}_{i_\alpha}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha}).$$

In order to have a continuum description, we will assume that the typical realizations of the microstates z are such that the hydrodynamic fields are continuous and differentiable functions of space.

The Hamiltonian (69) can be written in a continuum fashion as

$$H(z)=\int d\mathbf{r}\left(\frac{\mathbf{g}^2_{\mathbf{r}}(z)}{2\rho_{\mathbf{r}}(z)}+\hat{\boldsymbol{\epsilon}}_{\mathbf{r}}(z)\right)$$
$$+\frac{1}{2}\sum_{\alpha\beta}^{r}\int d\mathbf{r}\int d\mathbf{r}'\ \overline{\phi}^{\alpha\beta}_{\mathbf{r}\mathbf{r}'}n^\alpha_{\mathbf{r}}(z)n^\beta_{\mathbf{r}'}(z), \tag{76}$$

where we have introduced the total mass density field as

$$\rho_{\mathbf{r}}(z)=\sum_\alpha^r m_\alpha n^\alpha_{\mathbf{r}}(z). \tag{77}$$

Other dynamical invariants of the microscopic dynamics are the total momentum $\mathbf{P}(z)$ in Eq. (70) of the system, which can also be written in terms of the continuum variables (75),

$$\mathbf{P}(z)=\int d\mathbf{r}\ \mathbf{g}_{\mathbf{r}}(z), \tag{78}$$

and the total mass of each species,

$$M^\alpha(z)=\int d\mathbf{r}\ m_\alpha n^\alpha_{\mathbf{r}}(z). \tag{79}$$

Clearly, the energy function as defined in Eq. (51) is, for the fluid mixture,

$$E(x)=\int d\mathbf{r}\left(\frac{\mathbf{g}^2_{\mathbf{r}}}{2\rho_{\mathbf{r}}}+\hat{\boldsymbol{\epsilon}}_{\mathbf{r}}+\frac{1}{2}\sum_{\alpha\beta}^{r}n^\alpha_{\mathbf{r}}\int d\mathbf{r}'\ \overline{\phi}^{\alpha\beta}_{\mathbf{r}\mathbf{r}'}n^\beta_{\mathbf{r}'}\right). \tag{80}$$

The functional derivatives of the energy functional with respect to the hydrodynamic fields are the following:

$$\frac{\delta E}{\delta x}=\begin{pmatrix}\dfrac{\delta E}{\delta n_{\mathbf{r}}^{A}}\\ \dfrac{\delta E}{\delta n_{\mathbf{r}}^{B}}\\ \dfrac{\delta E}{\delta \mathbf{g}_{\mathbf{r}}}\\ \dfrac{\delta E}{\delta \hat{\epsilon}_{\mathbf{r}}}\end{pmatrix}=\begin{pmatrix}-m_A\dfrac{1}{2}\mathbf{v}_{\mathbf{r}}^2+\displaystyle\int d\mathbf{r}'\ \overline{\phi}_{\mathbf{r}\mathbf{r}'}^{AB}n_{\mathbf{r}}^{B}\\ -m_B\dfrac{1}{2}\mathbf{v}_{\mathbf{r}}^2+\displaystyle\int d\mathbf{r}'\ \overline{\phi}_{\mathbf{r}\mathbf{r}'}^{BA}n_{\mathbf{r}}^{A}\\ \mathbf{v}_{\mathbf{r}}\\ 1\end{pmatrix}, \tag{81}$$

where $\mathbf{v}_{\mathbf{r}}=\mathbf{g}_{\mathbf{r}}/\rho_{\mathbf{r}}$ is the velocity field.

B. Entropy of a fluid mixture in the van der Waals approximation

In Ref. 16 we have computed the entropy of a simple fluid by following a cell method first used by Green[6] and van Kampen.[17] Our approach in Ref. 16 has been to compute the probability distribution that a fluid system has a particular realization of the *full set* of discrete hydrodynamic variables. From this probability and through Eq. (59) we have inferred the entropy function. The method is easily generalized to the case of a fluid mixture. In this case, one computes the equilibrium probability functional that the system adopts a particular realization of the r density fields, the momentum density field, and the internal energy density field.

By following identical steps as for the simple fluid case[16] we have that Eq. (58) when specialized to the phase functions (62) becomes

$$P[x]=\int dz\ \rho^{\mathrm{eq}}(z)\prod_{\mu}\ \delta(\mathbf{P}_{\mu}(z)-\mathbf{P}_{\mu})\delta(\hat{\mathcal{E}}_{\mu}(z)-\mathcal{E}_{\mu})\times\chi(N_{\mu}^{A}(z)-N_{\mu}^{A})\chi(N_{\mu}^{B}(z)-N_{\mu}^{B}). \tag{82}$$

We assume that there are only two species $\alpha=A,B$, but the generalization to the r species is straightforward. The equilibrium distribution of the microscopic state z is given by

$$\rho^{\mathrm{eq}}(z)=\frac{1}{N^{A}!N^{B}!\Omega_0}\,\delta(\mathbf{P}(z)-\mathbf{P}_0)\,\delta(H(z)-E_0). \tag{83}$$

The functions $\chi(\cdots)$ in Eq. (82) are nonzero only for those microstates z that provide exactly N_{μ}^{A} particles of species A and N_{μ}^{B} particles of species B in each cell μ. There are

$$\frac{N^{A}!}{N_1^{A}!\cdots N_M^{A}!}\,\frac{N^{B}!}{N_1^{B}!\cdots N_M^{B}!} \tag{84}$$

equivalent ways of having the molecules with the prescribed distribution of particles in each cell and, therefore, we can write Eq. (82) as

$$P[x]=\frac{1}{\Omega_0}\,\delta(\mathbf{P}(x)-\mathbf{P}_0)\,\delta(E(x)-E_0)\,\chi\left(\sum_{\mu}\ N_{\mu}^{A}-N_0^{A}\right)\chi\left(\sum_{\mu}\ N_{\mu}^{B}-N_0^{B}\right)$$
$$\times\frac{1}{N_1^{A}!}\int_{\mathcal{V}_1}\underbrace{d\mathbf{q}^{A}\ldots d\mathbf{q}^{A}}_{N_1^{A}}\cdots\frac{1}{N_M^{A}!}\int_{\mathcal{V}_M}\underbrace{d\mathbf{q}^{A}\ldots d\mathbf{q}^{A}}_{N_M^{A}}\frac{1}{N_1^{B}!}\int_{\mathcal{V}_1}\underbrace{d\mathbf{q}^{B}\ldots d\mathbf{q}^{B}}_{N_1^{B}}\cdots\frac{1}{N_M^{B}!}\int_{\mathcal{V}_M}\underbrace{d\mathbf{q}^{B}\ldots d\mathbf{q}^{B}}_{N_M^{B}}$$
$$\times\int d\mathbf{p}\prod_{\mu}^{M}\ \delta\left(\sum_{\alpha}\sum_{i_{\mu}^{\alpha}}^{N_{\mu}^{\alpha}}\mathbf{p}_{i_{\mu}^{\alpha}}-\mathbf{P}_{\mu}\right)\delta\left(\sum_{\alpha}\sum_{i_{\mu}^{\alpha}}^{N_{\mu}^{\alpha}}\left(\frac{m_{\alpha}}{2}\left(\frac{\mathbf{p}_{i_{\mu}^{\alpha}}}{m_{\alpha}}-\mathbf{v}_{\mu}\right)^2+\hat{\phi}_{i_{\mu}^{\alpha}}\right)-\hat{\mathcal{E}}_{\mu}\right). \tag{85}$$

Here, N_0^{α} is the total number of molecules of species α, E_0 is the total energy of the system, and $\mathbf{P}_0$ is the total momentum of the system. We have introduced the functions $\chi(\Sigma_{\mu}N_{\mu}^{\alpha}-N^{\alpha})$, which take the value 1 if its argument is zero and zero otherwise in order to encompass the fact that $P[x]$ is zero if the total number of molecules of specie α does not exactly coincide with N_0^{α}.

Our aim now is to decouple the multiple integral (85) *by cells*. Note that the momentum integrals trivially decouple. The term that hinders the decoupling of the position integrals is the potential energy. This potential energy can be decomposed into two parts, one that accounts for the interaction of particles within cell μ plus another that accounts for the interaction of particles of cell μ with particles in different cells ν. Mathematically,

$$\sum_{\alpha}\sum_{i_{\mu}^{\alpha}}^{N_{\mu}^{\alpha}}\hat{\phi}_{i_{\mu}^{\alpha}}=\frac{1}{2}\sum_{\alpha\beta}\sum_{i_{\mu}^{\alpha}}^{N_{\mu}^{\alpha}}\sum_{j_{\mu}^{\beta}}^{N_{\mu}^{\beta}}\hat{\phi}_{i_{\mu}^{\alpha}j_{\mu}^{\beta}}+\frac{1}{2}{\sum_{\nu}}'\left(\sum_{\alpha\beta}\sum_{i_{\mu}^{\alpha}}^{N_{\mu}^{\alpha}}\sum_{j_{\nu}^{\beta}}^{N_{\nu}^{\beta}}\hat{\phi}_{i_{\mu}^{\alpha}j_{\nu}^{\beta}}\right). \tag{86}$$

In this expression, the prime in the term Σ_{ν}' denotes that this sum involves coordinates of particles of cells ν *different* from μ. This last term is the one that hinders the decoupling of the multiple integral in cells. This term is actually a surface energy due to the hard-core interaction between neighboring cells. We will neglect this contribution in front of the ''bulk''

contribution represented by the first term of the left-hand side of Eq. (86). In this way, we can decouple the integrals in Eq. (82) by cells with the result

$$P[x]=\frac{1}{\Omega_0}\,\delta(\mathbf{P}(x)-\mathbf{P}_0)\,\delta(E(x)-E_0)\prod_{\alpha}^{r}\,\chi\left(\sum_{\mu}\,N_{\mu}^{\alpha}-N^{\alpha}\right)\times\prod_{\mu}^{M}\,\hat{\Omega}(N_{\mu}^{A},N_{\mu}^{B},\hat{\mathcal{E}}_{\mu},\mathcal{V}_{\mu}),\tag{87}$$

where

$$\hat{\Omega}(N^{A},N^{B},\hat{\mathcal{E}},V)=\frac{1}{N^{A}!}\int_{V}\underbrace{d\mathbf{q}^{A}\ldots d\mathbf{q}^{A}}_{N^{A}}\int\underbrace{d\mathbf{p}^{A}\ldots d\mathbf{p}^{A}}_{N^{A}}\times\frac{1}{N^{B}!}\int_{V}\underbrace{d\mathbf{q}^{B}\ldots d\mathbf{q}^{B}}_{N^{B}}\int\underbrace{d\mathbf{p}^{B}\ldots d\mathbf{p}^{B}}_{N^{B}}\times\delta\left(\sum_{\alpha}^{N_{\alpha}}\sum_{i_{\alpha}}\mathbf{p}_{i_{\alpha}}\right)\times\delta\left(\sum_{\alpha}^{N_{\alpha}}\sum_{i_{\alpha}}\left(\frac{\mathbf{p}_{i_{\alpha}}^{2}}{2m_{\alpha}}+\hat{\phi}_{i_{\alpha}}\right)-\hat{\mathcal{E}}\right)\tag{88}$$

where we have made a Galilean change of variables $\mathbf{p}_{i_{\alpha}}\rightarrow\mathbf{p}_{i_{\alpha}}+m_{\alpha}\mathbf{v}_{\mu}$.

We introduce the usual definition of the entropy of a macroscopic system containing N_A,N_B particles interacting with a hard-core potential in a volume V and with total energy $\hat{\mathcal{E}}$, that is,

$$\hat{S}(N_A,N_B,\hat{\mathcal{E}},V)=k_B\ln\hat{\Omega}(N_A,N_B,\hat{\mathcal{E}},V).\tag{89}$$

In this way, the distribution function of the hydrodynamic variables for a fluid mixture at equilibrium is given by

$$P[x]=\frac{1}{\Omega_0}\,\delta(\mathbf{P}(x)-\mathbf{P}_0)\,\delta(E(x)-E_0)\prod_{\alpha}^{r}\,\chi\left(\sum_{\mu}\,N_{\mu}^{\alpha}-N^{\alpha}\right)\times\exp\left\{\sum_{\mu}^{M}\,\frac{1}{k_B}\hat{S}(N_{\mu}^{A},N_{\mu}^{B},\hat{\mathcal{E}}_{\mu},\mathcal{V}_{\mu})\right\}.\tag{90}$$

By comparing Eq. (90) with the general expression (59), we can extract the explicit form of the entropy of the system at the level of hydrodynamic variables, which for a binary mixture $\alpha=A,B$ is

$$S(x)=\sum_{\mu}^{M}\,\hat{S}(N_{\mu}^{A},N_{\mu}^{B},\hat{\mathcal{E}}_{\mu},\mathcal{V}_{\mu}).\tag{91}$$

This result may appear at first sight as deceptively simple, and one may wonder what is the need to go to the detailed calculation of the probability functional $P[x]$ presented above to derive Eq. (91). At the end of the day, one could say that the entropy is an additive quantity, and therefore, the total entropy of the system cannot be anything but Eq. (91). Yet this type of reasoning is not without hazard as it strongly depends on the type of hydrodynamic variables one is using. Actually, Eq. (91) says much more than simply "the entropy is additive." It states that the total entropy of the system is the sum of the entropies of a *hard-core* system, evaluated at the *hard-core* internal energy. That only hard-core quantities enter into the definition of the entropy is not a trivial result.

By using the fact that $\hat{S}$ is a first order function of its arguments, we can write

$$\hat{S}(N_A,N_B,\hat{\mathcal{E}},V)=V\hat{s}(n^{A},n^{B},\hat{\boldsymbol{\epsilon}})\tag{92}$$

and then Eq. (91) admits the continuum notation

$$S(x)=\int d\mathbf{r}\;\hat{s}(n_{\mathbf{r}}^{A},n_{\mathbf{r}}^{B},\hat{\boldsymbol{\epsilon}}_{\mathbf{r}}).\tag{93}$$

Note that behind the property (92) the thermodynamic limit is implicitly assumed. In this way, we are assuming that the size of the cell μ is much larger than the range of the hard-core potential. Note also the remark previous to Eq. (67). Taken together, these remarks imply that the size of the cell has to be large in front of the range of the hard-core potential, but small in front of the range of the long-ranged part of the potential.

The functional derivatives of the entropy functional with respect to the hydrodynamic fields are

$$\frac{\delta S}{\delta x}=\begin{pmatrix}-\dfrac{\hat{\mu}_{\mathbf{r}}^{A}}{\hat{T}_{\mathbf{r}}}\\[2mm]-\dfrac{\hat{\mu}_{\mathbf{r}}^{B}}{\hat{T}_{\mathbf{r}}}\\[2mm]0\\[2mm]\dfrac{1}{\hat{T}_{\mathbf{r}}}\end{pmatrix},\tag{94}$$

where we have introduced the usual definition of the intensive parameters (chemical potentials $\hat{\mu}^{\alpha}$ of species α and temperature $\hat{T}$) of the hard-core system:

$$\frac{1}{\hat{T}}=\frac{\partial}{\partial\hat{\boldsymbol{\epsilon}}}\hat{\mathrm{s}}(n^{A},n^{B},\hat{\boldsymbol{\epsilon}}),\qquad\frac{\hat{\mu}^{A}}{\hat{T}}=-\frac{\partial}{\partial n^{A}}\hat{\mathrm{s}}(n^{A},n^{B},\hat{\boldsymbol{\epsilon}}),\qquad\frac{\hat{\mu}^{B}}{\hat{T}}=-\frac{\partial}{\partial n^{B}}\hat{\mathrm{s}}(n^{A},n^{B},\hat{\boldsymbol{\epsilon}}).\tag{95}$$

The property (92) and the definitions (95) have as a consequence the Gibbs–Duhem relation[18]

$$\sum_{\alpha}\,n^{\alpha}d\left(\frac{\hat{\mu}^{\alpha}}{\hat{T}}\right)-\hat{\boldsymbol{\epsilon}}d\left(\frac{1}{\hat{T}}\right)-d\left(\frac{\hat{P}}{\hat{T}}\right)=0,\tag{96}$$

where $\hat{P}$ is the pressure of the hard-core system. The Gibbs–Duhem relation can be written in the continuum form

$$\sum_{\alpha}\,n_{\mathbf{r}}^{\alpha}\boldsymbol{\nabla}\left(\frac{\hat{\mu}_{\mathbf{r}}}{\hat{T}_{\mathbf{r}}}\right)-\hat{\boldsymbol{\epsilon}}_{\mathbf{r}}\boldsymbol{\nabla}\left(\frac{1}{\hat{T}_{\mathbf{r}}}\right)-\boldsymbol{\nabla}\left(\frac{\hat{P}_{\mathbf{r}}}{\hat{T}_{\mathbf{r}}}\right)=0,\tag{97}$$

where all the intensive parameters are regarded as functions of $n_{\mathbf{r}}^{\alpha}, \hat{\epsilon}_{\mathbf{r}}$.

C. Constrained averages

In the microscopic definitions of the reversible and irreversible operators in Eqs. (49) and (53), the constrained averages defined in general in Eq. (46) appear. We present in this section the calculation of the constrained average of an arbitrary *local function* G_μ of the form

$$G_\mu(z)=\sum_\alpha \sum_{i_\alpha} g_{i_\alpha}(z)\overline{\delta}(\mathbf{q}_{i_\alpha}-\mathbf{r}_\mu), \tag{98}$$

where g_{i_α} is an arbitrary function of the coordinates $\mathbf{r}_{i_\alpha}$ and momenta $\mathbf{p}_{i_\alpha}$ of particle i of specie α. We say that G_μ is *local* because it only involves the coordinates of those particles that are in cell μ.

The general definition of the constrained average (46) becomes, for the case that the relevant variables x are Eqs. (62),

$$\langle G_\mu\rangle^x=\exp\{-S(x)/k_B\}\int dz\; G_\mu(z)\prod_\nu \delta(\mathbf{P}_\nu(z)-\mathbf{P}_\nu) \times\delta(\hat{\mathcal{E}}_\nu(z)-\mathcal{E}_\nu)\chi(N_\nu^A(z)-N_\nu^A)\chi(N_\nu^B(z)-N_\nu^B). \tag{99}$$

Under the assumption of negligible hard-core interaction between neighboring cells, we can write the above average as simply

$$\begin{aligned}\langle G_\mu\rangle^x=&\exp\{-\hat{S}(N_\mu^A,N_\mu^B,\hat{\mathcal{E}}_\mu,V_\mu)/k_B\}\\ &\times\frac{1}{N_\mu^A!}\frac{1}{N_\mu^B!}\int_{\mathcal{V}_\mu}\underbrace{d\mathbf{q}^A\ldots d\mathbf{q}^A}_{N_\mu^A}\int_{\mathcal{V}_\mu}\underbrace{d\mathbf{q}^B\ldots d\mathbf{q}^B}_{N_\mu^B}\\ &\times\int\underbrace{d\mathbf{p}^A\ldots d\mathbf{p}^A}_{N_\mu^A}\int\underbrace{d\mathbf{p}^B\ldots d\mathbf{p}^B}_{N_\mu^B}\\ &\times\frac{1}{\mathcal{V}_\mu}\left(\sum_\alpha\sum_{i_\mu^\alpha}^{N_\mu} g_{i_\mu^\alpha}\right)\delta\left(\sum_\alpha\sum_{i_\mu^\alpha}^{N_\mu^\alpha}\mathbf{p}_{i_\mu^\alpha}-\mathbf{P}_\mu\right)\\ &\times\delta\left(\sum_\alpha\sum_{i_\mu^\alpha}^{N_\mu^\alpha}\left(\frac{m_\alpha}{2}\left(\frac{\mathbf{p}_{i_\mu^\alpha}}{m_\alpha}-\mathbf{v}_\mu\right)^2+\hat{\phi}_{i_\mu^\alpha}\right)-\hat{\mathcal{E}}_\mu\right)\end{aligned} \tag{100}$$

where i_μ^α is the label of particles of type α that are in cell μ. By taking a Galilean transformation,

$$\begin{aligned}\langle G_\mu\rangle^x=&\exp\{-\hat{S}(N_\mu^A,N_\mu^B,\hat{\mathcal{E}}_\mu,V_\mu)/k_B\}\\ &\times\frac{1}{N_\mu^A!}\frac{1}{N_\mu^B!}\int_{\mathcal{V}_\mu}\underbrace{d\mathbf{q}^A\ldots d\mathbf{q}^A}_{N_\mu^A}\int_{\mathcal{V}_\mu}\underbrace{d\mathbf{q}^B\ldots d\mathbf{q}^B}_{N_\mu^B}\\ &\times\int\underbrace{d\mathbf{p}^A\ldots d\mathbf{p}^A}_{N_\mu^A}\int\underbrace{d\mathbf{p}^B\ldots d\mathbf{p}^B}_{N_\mu^B}\\ &\times\frac{1}{\mathcal{V}_\mu}\left(\sum_\alpha\sum_{i_\mu^\alpha}^{N_\mu}\mathcal{G}_\mu g_{i_\alpha^\mu}\right)\delta\left(\sum_\alpha\sum_{i_\mu^\alpha}^{N_\mu^\alpha}\mathbf{p}_{i_\mu^\alpha}\right)\\ &\times\delta\left(\sum_\alpha\sum_{i_\mu^\alpha}^{N_\mu^\alpha}\left(\frac{\mathbf{p}_{i_\mu^\alpha}^2}{2m_\alpha}+\hat{\phi}_{i_\mu^\alpha}\right)-\hat{\mathcal{E}}_\mu\right).\end{aligned} \tag{101}$$

In summary,

$$\langle G_\mu\rangle^x=\langle\mathcal{G}_\mu g_\mu(z)\rangle_\mu^{\mathrm{eq}}, \tag{102}$$

where $\langle\cdots\rangle_\mu^{\mathrm{eq}}$ is a usual equilibrium microcanonical average of a system at rest containing N_μ^α molecules of specie $\alpha=1,\ldots,r$ and a given energy $\hat{\mathcal{E}}_\mu$. Again, it should be remarked that the Hamiltonian that should be used in this equilibrium microcanonical average has only a hard-core potential. The function $g_\mu(z)$ in Eq. (102) is

$$g_\mu(z)=\frac{1}{\mathcal{V}_\mu}\sum_\alpha\sum_{i_\alpha}^{N_\mu^\alpha} g_{i_\mu^\alpha}, \tag{103}$$

and the Galilean operator $\mathcal{G}_\mu$ is defined through its action on an arbitrary phase function $A(z)$ as follows:

$$\begin{aligned}&\mathcal{G}_\mu A(\mathbf{q}_{i_\alpha},\mathbf{p}_{i_\alpha},\mathbf{q}_{i_\beta},\mathbf{p}_{i_\beta})\\ &\quad=A(\mathbf{q}_{i_\alpha},\mathbf{p}_{i_\alpha}+m^\alpha\mathbf{v}_\mu,\mathbf{q}_{i_\beta},\mathbf{p}_{i_\beta}+m^\beta\mathbf{v}_\mu).\end{aligned} \tag{104}$$

Equation (102) is a very important result as it reflects the concept of *local equilibrium*. The constrained average of a local function can be computed as an equilibrium microcanonical average in the rest frame and with the local values of the energy and number of particles.

D. Reversible dynamics

The elements of the reversible matrix L defined in Eq. (53) will have the following structure for a fluid mixture:

$$L_{\mathbf{r}\mathbf{r}'}^{xy}=\sum_\gamma\sum_{k_\gamma}\left\langle\frac{\partial x_{\mathbf{r}}}{\partial\mathbf{q}_{k_\gamma}}\cdot\frac{\partial y_{\mathbf{r}'}}{\partial\mathbf{p}_{k_\gamma}}-\frac{\partial x_{\mathbf{r}}}{\partial\mathbf{p}_{k_\gamma}}\cdot\frac{\partial y_{\mathbf{r}'}}{\partial\mathbf{q}_{k_\gamma}}\right\rangle^x, \tag{105}$$

where $x_{\mathbf{r}}, y_{\mathbf{r}}$ are any of the hydrodynamic fields. In order to compute the reversible matrix as defined in Eq. (53) it is necessary to compute previously the derivatives of the relevant variables with respect to the microstate. These derivatives are

$$\frac{\partial n^{\alpha}_{\mathbf{r}}(z)}{\partial \mathbf{q}_{k_\gamma}} = -\delta_{\alpha\gamma}\boldsymbol{\nabla}\overline{\delta}(\mathbf{r}-\mathbf{q}_{k_\gamma}),$$

$$\frac{\partial n^{\alpha}_{\mathbf{r}}(z)}{\partial \mathbf{p}_{k_\gamma}} = 0,$$

$$\frac{\partial \mathbf{g}_{\mathbf{r}}(z)}{\partial \mathbf{q}_{k_\gamma}} = -\mathbf{p}_{k_\gamma}\boldsymbol{\nabla}\overline{\delta}(\mathbf{r}-\mathbf{q}_{k_\gamma}), \tag{106}$$

$$\frac{\partial \mathbf{g}_{\mathbf{r}}(z)}{\partial \mathbf{p}_{k_\gamma}} = \mathbf{1}\overline{\delta}(\mathbf{r}-\mathbf{q}_{k_\gamma}),$$

$$\frac{\partial \hat{\boldsymbol{\epsilon}}_{\mathbf{r}}(z)}{\partial \mathbf{p}_{i_\gamma}} = \overline{\delta}(\mathbf{r}-\mathbf{q}_{k_\gamma})\left(\frac{\mathbf{p}_{k_\gamma}}{m_\gamma}-\mathbf{v}_{\mathbf{r}}\right),$$

where **1** is the unit tensor.

The calculation of the derivative of the internal energy density field with respect to the positions is a bit more involved. We first use

$$\frac{\partial \hat{\phi}_{i_\alpha j_\beta}}{\partial \mathbf{q}_{k_\gamma}} = -\hat{\mathbf{F}}_{i_\alpha j_\beta}(\delta_{\alpha\gamma}\delta_{i_\alpha k_\gamma}-\delta_{\beta\gamma}\delta_{j_\beta k_\gamma}), \tag{107}$$

where $\hat{\mathbf{F}}_{i_\alpha j_\beta}$ is the hard-core force that particle j of specie β exerts on particle i of specie α. In this way,

$$\frac{\partial \hat{\boldsymbol{\epsilon}}_{\mathbf{r}}(z)}{\partial \mathbf{q}_{k_\gamma}} = -\hat{\boldsymbol{\epsilon}}_{k_\gamma}\boldsymbol{\nabla}\overline{\delta}(\mathbf{r}-\mathbf{q}_{k_\gamma}),$$

$$-\frac{1}{2}\sum_{\beta}\sum_{j_\beta}\hat{\mathbf{F}}_{k_\gamma j_\beta}[\overline{\delta}(\mathbf{r}-\mathbf{q}_{k_\gamma})+\overline{\delta}(\mathbf{r}-\mathbf{q}_{j_\beta})]. \tag{108}$$

We can now obtain the following elements of the matrix L:

$$L^{n^\alpha n^\beta}_{\mathbf{r}\mathbf{r}'} = 0,$$

$$L^{n^\alpha \mathbf{g}}_{\mathbf{r}\mathbf{r}'} = n^{\alpha}_{\mathbf{r}'}\boldsymbol{\nabla}'\overline{\delta}_{\mathbf{r}\mathbf{r}'},$$

$$L^{n^\alpha \hat{\boldsymbol{\epsilon}}}_{\mathbf{r}\mathbf{r}'} = 0,$$

$$L^{\mathbf{g}\mathbf{g}}_{\mathbf{r}\mathbf{r}'} = [\mathbf{g}_{\mathbf{r}'}\boldsymbol{\nabla}'\overline{\delta}_{\mathbf{r}\mathbf{r}'}+\boldsymbol{\nabla}'\overline{\delta}_{\mathbf{r}\mathbf{r}'}\mathbf{g}_{\mathbf{r}}], \tag{109}$$

$$L^{\mathbf{g}\hat{\boldsymbol{\epsilon}}}_{\mathbf{r}\mathbf{r}'} = \hat{\boldsymbol{\epsilon}}_{\mathbf{r}}\boldsymbol{\nabla}'\overline{\delta}_{\mathbf{r}\mathbf{r}'}+\hat{\mathbf{F}}_{\mathbf{r}\mathbf{r}'},$$

$$L^{\hat{\boldsymbol{\epsilon}}\hat{\boldsymbol{\epsilon}}}_{\mathbf{r}\mathbf{r}'} = 0.$$

Here, $\overline{\delta}_{\mathbf{r}\mathbf{r}'}$ is a shorthand for the coarse-grained delta function, whereas

$$\boldsymbol{\nabla}'\overline{\delta}_{\mathbf{r}\mathbf{r}'} = \frac{\partial}{\partial \mathbf{r}'}\overline{\delta}(\mathbf{r}-\mathbf{r}'). \tag{110}$$

In order to obtain Eqs. (109) we have used the following results:

$$\left\langle \sum_{k_\beta}\boldsymbol{\nabla}\overline{\delta}(\mathbf{r}-\mathbf{q}_{k_\beta})\overline{\delta}(\mathbf{r}'-\mathbf{q}_{k_\beta})\right\rangle^{x} = \boldsymbol{\nabla}\delta_{\mathbf{r}\mathbf{r}'}\langle n^{\beta}_{\mathbf{r}'}(z)\rangle^{x} = \boldsymbol{\nabla}\delta_{\mathbf{r}\mathbf{r}'}n^{\beta}_{\mathbf{r}'},$$

$$\left\langle \sum_{\beta}\sum_{k_\beta}\overline{\delta}(\mathbf{r}'-\mathbf{q}_{k_\beta})\left(\frac{\mathbf{p}_{k_\beta}}{m_\beta}-\mathbf{v}_{\mathbf{r}'}\right)\right\rangle^{x} = 0. \tag{111}$$

The first identity is due to the fact that we are computing the average of the density field constrained to produce a particular value of the density field (and the rest of hydrodynamic fields denoted symbolically by x). The second identity in Eqs. (111) is an instance of Eq. (102) together with the fact that the equilibrium average of the momentum is zero. The vanishing of $L^{\hat{\boldsymbol{\epsilon}}\hat{\boldsymbol{\epsilon}}}_{\mathbf{r}\mathbf{r}'}$ in Eqs. (109) is due to the same reason.

In Eqs. (109) we have introduced the following coarse-grained force between two points of the fluid:

$$\hat{\mathbf{F}}_{\mathbf{r}\mathbf{r}'} = \left\langle \frac{1}{2}\sum_{\gamma\beta}\sum_{k_\gamma j_\beta}\hat{\mathbf{F}}_{k_\gamma j_\beta}\delta(\mathbf{r}-\mathbf{q}_{k_\gamma})\sum_{k_\gamma\in\hat{\mathbf{F}}_{\mathbf{r}}}[\overline{\delta}(\mathbf{r}'-\mathbf{q}_{k_\gamma}) + \overline{\delta}(\mathbf{r}'-\mathbf{q}_{j_\beta})]\right\rangle^{x} - \sum_{\gamma}\sum_{k_\gamma}\langle(\mathbf{p}_{k_\gamma}-m_\gamma\mathbf{v}_{\mathbf{r}'}) \times(\mathbf{p}_{k_\gamma}-m_\gamma\mathbf{v}_{\mathbf{r}'})\rangle^{x}\boldsymbol{\nabla}\overline{\delta}_{\mathbf{r}\mathbf{r}'}. \tag{112}$$

By following the pioneering work by Irwing and Kirkwood,[31] the usual treatment of this term (112) is to perform a Taylor expansion of the delta function in the form

$$\overline{\delta}(\mathbf{r}-\mathbf{q}_{k_\gamma})-\overline{\delta}(\mathbf{r}-\mathbf{q}_{j_\beta}) = -\mathbf{q}_{k_\gamma j_\beta}\boldsymbol{\nabla}\overline{\delta}(\mathbf{r}-\mathbf{q}_{k_\gamma}). \tag{113}$$

By inserting this expansion into Eq. (112) we obtain

$$\hat{\mathbf{F}}_{\mathbf{r}\mathbf{r}'} = \langle\mathcal{G}^{-1}\hat{\boldsymbol{\sigma}}_{\mathbf{r}'}\rangle^{x}\boldsymbol{\nabla}'\overline{\delta}_{\mathbf{r}\mathbf{r}'}. \tag{114}$$

Here $\mathcal{G}^{-1}_{\mathbf{r}}$ is the inverse of the Galilean operator introduced in Eq. (104) (where we have changed the discrete label μ by the continuum label $\mathbf{r}$). The inverse operator is obtained by reversing the sign of the velocity field. We have introduced in Eq. (114) the usual microscopic expression for the stress tensor:

$$\mathcal{G}^{-1}_{\mathbf{r}}\hat{\boldsymbol{\sigma}}_{\mathbf{r}} = \sum_{\alpha}\sum_{i_\alpha} m_\alpha\left(\frac{\mathbf{p}_{i_\alpha}}{m_\alpha}-\mathbf{v}_{\mathbf{r}}\right)\left(\frac{\mathbf{p}_{i_\alpha}}{m_\alpha}-\mathbf{v}_{\mathbf{r}}\right)\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha}) + \frac{1}{2}\sum_{\gamma\beta}\sum_{k_\gamma j_\beta}\hat{\mathbf{F}}_{k_\gamma j_\beta}\mathbf{q}_{k_\gamma j_\beta}\overline{\delta}(\mathbf{r}-r_{k_\gamma}). \tag{115}$$

By collecting all the elements of the matrix L in Eqs. (109), we can finally write

$$L_{\mathbf{r}\mathbf{r}'}=\begin{pmatrix} 0 & 0 & n^A_{\mathbf{r}'}\boldsymbol{\nabla}'\overline{\delta}_{\mathbf{r}\mathbf{r}'} & 0 \\ 0 & 0 & n^B_{\mathbf{r}'}\boldsymbol{\nabla}'\overline{\delta}_{\mathbf{r}\mathbf{r}'} & 0 \\ n^A_{\mathbf{r}}\boldsymbol{\nabla}'\overline{\delta}_{\mathbf{r}\mathbf{r}'} & n^B_{\mathbf{r}}\boldsymbol{\nabla}'\overline{\delta}_{\mathbf{r}\mathbf{r}'} & \mathbf{g}_{\mathbf{r}'}\boldsymbol{\nabla}'\overline{\delta}_{\mathbf{r}\mathbf{r}'}+\boldsymbol{\nabla}'\overline{\delta}_{\mathbf{r}\mathbf{r}'}\mathbf{g}_{\mathbf{r}} & \hat{\boldsymbol{\epsilon}}_{\mathbf{r}}\boldsymbol{\nabla}'\overline{\delta}_{\mathbf{r}\mathbf{r}'}+\langle\mathcal{G}^{-1}_{\mathbf{r}'}\hat{\boldsymbol{\sigma}}_{\mathbf{r}'}\rangle^x\boldsymbol{\nabla}'\overline{\delta}_{\mathbf{r}\mathbf{r}'} \\ 0 & 0 & \hat{\boldsymbol{\epsilon}}_{\mathbf{r}'}\boldsymbol{\nabla}'\overline{\delta}_{\mathbf{r}\mathbf{r}'}+\langle\mathcal{G}^{-1}_{\mathbf{r}}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\rangle^x\boldsymbol{\nabla}'\overline{\delta}_{\mathbf{r}\mathbf{r}'} & 0 \end{pmatrix}. \tag{116}$$

The only unknown quantity in this matrix is $\langle\mathcal{G}^{-1}_{\mathbf{r}}\hat{\boldsymbol{\sigma}}_{\mathbf{r}'}\rangle^x\boldsymbol{\nabla}'\overline{\delta}_{\mathbf{r}\mathbf{r}'}$. We have two routes for computing this quantity. The first one is to use the result (102) in order to perform explicitly the constrained average of the microscopic stress tensor. The second is to use the degeneracy $L\nabla S=0$ presented in Eq. (57). Both routes provide the same answer and we illustrate the second, which is the simplest one. The degeneracy $L\nabla S=0$ becomes, in the fluid mixture case,

$$\int d\mathbf{r}'\left[\sum_\alpha n^\alpha_{\mathbf{r}}\boldsymbol{\nabla}'\overline{\delta}_{\mathbf{r}\mathbf{r}'}\left(-\frac{\hat{\mu}^\alpha_{\mathbf{r}'}}{\hat{T}_{\mathbf{r}'}}\right)+\hat{\boldsymbol{\epsilon}}_{\mathbf{r}}\boldsymbol{\nabla}'\overline{\delta}_{\mathbf{r}\mathbf{r}'}\frac{1}{\hat{T}_{\mathbf{r}'}}+\langle\mathcal{G}^{-1}_{\mathbf{r}'}\hat{\boldsymbol{\sigma}}_{\mathbf{r}'}\rangle^x\boldsymbol{\nabla}'\overline{\delta}_{\mathbf{r}\mathbf{r}'}\frac{1}{\hat{T}_{\mathbf{r}'}}\right]=0 \tag{117}$$

or, by performing the integrals over the delta functions,

$$\sum_\alpha n^\alpha_{\mathbf{r}}\boldsymbol{\nabla}\left(\frac{\hat{\mu}_{\mathbf{r}}}{\hat{T}_{\mathbf{r}}}\right)-\hat{\boldsymbol{\epsilon}}_{\mathbf{r}}\boldsymbol{\nabla}\left(\frac{1}{\hat{T}_{\mathbf{r}}}\right)-\boldsymbol{\nabla}\left(\frac{\langle\mathcal{G}^{-1}_{\mathbf{r}}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\rangle^x}{\hat{T}_{\mathbf{r}}}\right)=0. \tag{118}$$

By comparing with the Gibbs–Duhem relation (97) we readily obtain

$$\langle\mathcal{G}^{-1}_{\mathbf{r}}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\rangle^x=\hat{P}_{\mathbf{r}}\mathbf{1}. \tag{119}$$

We are now in position to write the reversible part of the dynamics $\dot{x}|_{\mathrm{rev}}=L\nabla E$ by using Eq. (116) with Eqs. (118) and (81). The balance of mass equations take the form

$$\partial_t n^\alpha_{\mathbf{r}}=-\boldsymbol{\nabla}\mathbf{v}_{\mathbf{r}}n^\alpha_{\mathbf{r}}. \tag{120}$$

The momentum balance equation becomes

$$\partial_t\mathbf{g}_{\mathbf{r}}=-\boldsymbol{\nabla}\cdot(\mathbf{g}_{\mathbf{r}}\mathbf{v}_{\mathbf{r}})-\boldsymbol{\nabla}\hat{P}_{\mathbf{r}}-\sum_\alpha n^\alpha_{\mathbf{r}}\boldsymbol{\nabla}\frac{\delta\overline{\Phi}}{\delta n^\alpha_{\mathbf{r}}}, \tag{121}$$

where the pressure is given by the equation of state $\hat{P}_{\mathbf{r}}=\hat{P}(n^A_{\mathbf{r}},n^B_{\mathbf{r}},\hat{\boldsymbol{\epsilon}}_{\mathbf{r}})$. We have introduced in Eq. (121) the total mean-field potential energy given by

$$\overline{\Phi}=\frac{1}{2}\sum_{\alpha\beta}\int d\mathbf{r}\,\mathbf{r}'n^\alpha_{\mathbf{r}}n^\beta_{\mathbf{r}'}\overline{\phi}^{\alpha\beta}_{\mathbf{r}\mathbf{r}'}. \tag{122}$$

Note that Eq. (121) can also be written as

$$\partial_t\mathbf{g}_{\mathbf{r}}=-\boldsymbol{\nabla}\cdot(\mathbf{g}_{\mathbf{r}}\mathbf{v}_{\mathbf{r}})-\boldsymbol{\nabla}\hat{P}_{\mathbf{r}}+\sum_\alpha n^\alpha_{\mathbf{r}}\overline{\mathbf{F}}^\alpha_{\mathbf{r}}, \tag{123}$$

where

$$\overline{\mathbf{F}}^\alpha_{\mathbf{r}}=-\boldsymbol{\nabla}\frac{\delta\overline{\Phi}}{\delta n^\alpha_{\mathbf{r}}}=\sum_\beta\int d\mathbf{r}'\;\overline{\mathbf{F}}^{\alpha\beta}_{\mathbf{r}\mathbf{r}'}n^\beta_{\mathbf{r}'} \tag{124}$$

and $\overline{\mathbf{F}}^{\alpha\beta}_{\mathbf{r}\mathbf{r}'}$ is the long-range attractive force that a molecule of species β in $\mathbf{r}'$ exerts on a molecule of species α in $\mathbf{r}$. Finally, the energy equation is given by

$$\partial_t\hat{\boldsymbol{\epsilon}}_{\mathbf{r}}=-\boldsymbol{\nabla}\cdot(\mathbf{v}_{\mathbf{r}}\hat{\boldsymbol{\epsilon}}_{\mathbf{r}})-\hat{P}_{\mathbf{r}}\boldsymbol{\nabla}\cdot\mathbf{v}_{\mathbf{r}}. \tag{125}$$

Equations (120), (123), and (125) are the corresponding Euler equations for a phase-separating fluid mixture.

E. Irreversible dynamics

In order to compute the irreversible matrix M in Eq. (49), we need to compute the time derivatives $iLX(z)$ of the relevant variables. A straightforward calculation leads to the microscopic mass balance equation

$$iLn^\alpha_{\mathbf{r}}(z)=-\boldsymbol{\nabla}\cdot\frac{1}{m_\alpha}\mathbf{g}^\alpha_{\mathbf{r}}(z), \tag{126}$$

where we have introduced

$$\mathbf{g}^\alpha_{\mathbf{r}}(z)=\sum_{i_\alpha}\mathbf{p}_{i_\alpha}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha}) \tag{127}$$

to be distinguished from $\mathbf{g}_{\mathbf{r}}$ in Eq. (75). Actually we have

$$\mathbf{g}_{\mathbf{r}}(z)=\sum_\alpha^r\mathbf{g}^\alpha_{\mathbf{r}}(z). \tag{128}$$

The time derivative of the momentum density field can be written as

$$iL\mathbf{g}_{\mathbf{r}}=-\boldsymbol{\nabla}\cdot\sum_\alpha\sum_{i_\alpha}\mathbf{p}_{i_\alpha}\mathbf{v}_{i_\alpha}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha})+\sum_{\alpha\beta}\sum_{i_\alpha j_\beta}\mathbf{F}_{i_\alpha j_\beta}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha}). \tag{129}$$

Let us analyze the force term in Eq. (129). Under the separation of the potential into a short-range repulsive core plus a long-range attractive tail, we may write, for the forces,

$$\mathbf{F}_{i_\alpha j_\beta}=\hat{\mathbf{F}}_{i_\alpha j_\beta}+\overline{\mathbf{F}}_{i_\alpha j_\beta}. \tag{130}$$

The last term in Eq. (129) can then be written as

$$\begin{aligned}\sum_{\alpha\beta}\sum_{i_\alpha j_\beta}\mathbf{F}_{i_\alpha j_\beta}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha})&=\sum_{\alpha\beta}\sum_{i_\alpha j_\beta}\hat{\mathbf{F}}_{i_\alpha j_\beta}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha})+\sum_{\alpha\beta}\sum_{i_\alpha j_\beta}\overline{\mathbf{F}}_{i_\alpha j_\beta}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha})\\&\approx\sum_{\alpha\beta}\sum_{i_\alpha j_\beta}\hat{\mathbf{F}}_{i_\alpha j_\beta}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha})+\sum_{\alpha\beta}\int d\mathbf{r}'\;\overline{\mathbf{F}}^{\alpha\beta}_{\mathbf{r}\mathbf{r}'}n^\alpha_{\mathbf{r}}(z)n^\beta_{\mathbf{r}'}(z),\end{aligned} \tag{131}$$

where we have used the long-range nature of the last term. Note that we are not allowed to perform a similar approximation for the short-range part of the force, due to the finite support of the coarse-grained delta functions.

The time derivative of the internal energy density field is straightforward to obtain. It can be expressed as follows:

$$
\begin{aligned}
iL\hat{\epsilon}_{\mathbf{r}} =& -\boldsymbol{\nabla}\cdot\sum_{\alpha}\sum_{i_\alpha}\mathbf{v}_{i_\alpha}\hat{\epsilon}_{i_\alpha}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha}) - \sum_{\alpha}\sum_{i_\alpha} i_\alpha m_\alpha(\mathbf{v}_{i_\alpha}-\mathbf{v}_{\mathbf{r}}) \\
&\times(\mathbf{v}_{i_\alpha}-\mathbf{v}_{\mathbf{r}})\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha}):\nabla\mathbf{v}_{\mathbf{r}} + \frac{1}{2}\sum_{\alpha\beta}\sum_{i_\alpha j_\beta}\hat{\mathbf{F}}_{i_\alpha j_\beta} \\
&\cdot(\mathbf{v}_{i_\alpha}+\mathbf{v}_{j_\beta})\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha}) - \mathbf{v}_{\mathbf{r}}\cdot\sum_{\alpha\beta}\sum_{i_\alpha j_\beta}\hat{\mathbf{F}}_{i_\alpha j_\beta}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha}) \\
&+\sum_{\alpha}\sum_{i_\alpha}(\mathbf{v}_{i_\alpha}-\mathbf{v}_{\mathbf{r}})\cdot\overline{\mathbf{F}}_{i_\alpha}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha}). \qquad (132)
\end{aligned}
$$

The second term on the right-hand side of Eq. (132) can be written by using symmetry properties and the Taylor expansion (113) as

$$
\begin{aligned}
&\frac{1}{2}\sum_{\alpha\beta}\sum_{i_\alpha j_\beta}\hat{\mathbf{F}}_{i_\alpha j_\beta}\cdot(\mathbf{v}_{i_\alpha}+\mathbf{v}_{j_\beta})\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha}) \\
&\quad=\frac{1}{4}\sum_{\alpha\beta}\sum_{i_\alpha j_\beta}\hat{\mathbf{F}}_{i_\alpha j_\beta}\cdot(\mathbf{v}_{i_\alpha}+\mathbf{v}_{j_\beta})[\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha})-\overline{\delta}(\mathbf{r}-\mathbf{q}_{j_\beta})] \\
&\quad=-\boldsymbol{\nabla}\cdot\frac{1}{4}\sum_{\alpha\beta}\sum_{i_\alpha j_\beta}\hat{\mathbf{F}}_{i_\alpha j_\beta}\cdot(\mathbf{v}_{i_\alpha}+\mathbf{v}_{j_\beta})\mathbf{q}_{i_\alpha j_\beta}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha}). \qquad (133)
\end{aligned}
$$

We need now to compute the constrained averages $\langle iLX\rangle^x$ that appear in δiLX. The simplest procedure is to realize that these constrained averages are actually the reversible part of the dynamics, as is shown in Eq. (45). We have already computed this reversible part of the dynamics through Eq. (45), which leads to the results (120), (121), and (125). Therefore, after some algebra, we have the following realization of $\delta iLX = iLX - \langle iLX\rangle^x$ for the case of the hydrodynamic variables:

$$
\begin{aligned}
\delta iLn^{\alpha}_{\mathbf{r}} =& -\boldsymbol{\nabla}\cdot\left(\mathcal{G}^{-1}_{\mathbf{r}}\frac{\mathbf{g}^{\alpha}_{\mathbf{r}}(z)}{m_\alpha}\right), \\
\delta iL\mathbf{g}_{\mathbf{r}} =& -\boldsymbol{\nabla}\cdot\mathcal{G}^{-1}_{\mathbf{r}}(\hat{\boldsymbol{\sigma}}_{\mathbf{r}}(z)-\hat{P}_{\mathbf{r}}\mathbf{1}) - \boldsymbol{\nabla}\cdot\mathbf{v}_{\mathbf{r}}\mathbf{v}_{\mathbf{r}}\sum_{\alpha}[n^{\alpha}_{\mathbf{r}}(z)-n^{\alpha}_{\mathbf{r}}] \\
&-\nabla\mathbf{v}_{\mathbf{r}}[\mathbf{g}_{\mathbf{r}}(z)-\mathbf{g}_{\mathbf{r}}] + \int d\mathbf{r}\,\overline{\mathbf{F}}_{\mathbf{r}\mathbf{r}'}[n^{\alpha}_{\mathbf{r}}(z)n^{\beta}_{\mathbf{r}'}(z)-n^{\alpha}_{\mathbf{r}}n^{\beta}_{\mathbf{r}'}], \qquad (134) \\
\delta iL\hat{\epsilon}_{\mathbf{r}} =& -\boldsymbol{\nabla}\cdot\mathbf{v}_{\mathbf{r}}[\hat{\epsilon}_{\mathbf{r}}(z)-\hat{\epsilon}_{\mathbf{r}}] + [\hat{\boldsymbol{\sigma}}_{\mathbf{r}}(z)-\hat{P}_{\mathbf{r}}\mathbf{1}]:\boldsymbol{\nabla}\mathbf{v}_{\mathbf{r}} - \boldsymbol{\nabla} \\
&\cdot(\mathcal{G}^{-1}\mathbf{J}^{q}_{\mathbf{r}}) + \sum_{\alpha}\left(\mathcal{G}^{-1}_{\mathbf{r}}\frac{\mathbf{g}^{\alpha}_{\mathbf{r}}(z)}{m_\alpha}\right)\cdot\overline{\mathbf{F}}^{\alpha}_{\mathbf{r}}(z).
\end{aligned}
$$

Note that these expressions have the form

$$
\delta iLX = \widetilde{\delta} iLX + F[X(z)-X], \qquad (135)
$$

where F is some function. The last term in Eq. (135) that involves the relevant variables themselves will vanish in any constrained average and, in particular, in the calculation of the matrix M. Therefore, we can omit these terms. The final result can then be expressed in the form

$$
\begin{aligned}
\delta iLn^{\alpha}_{\mathbf{r}} =& -\boldsymbol{\nabla}\cdot(\mathcal{G}^{-1}_{\mathbf{r}}\mathbf{J}^{\alpha}_{\mathbf{r}}(z)), \\
\delta iL\mathbf{g}_{\mathbf{r}} =& -\boldsymbol{\nabla}\cdot(\mathcal{G}^{-1}_{\mathbf{r}}(\hat{\boldsymbol{\sigma}}_{\mathbf{r}}(z)-\hat{P}_{\mathbf{r}}\mathbf{1})), \qquad (136) \\
\delta iL\hat{\epsilon}_{\mathbf{r}} =& \mathcal{G}^{-1}_{\mathbf{r}}(\hat{\boldsymbol{\sigma}}_{\mathbf{r}}(z)-\hat{P}_{\mathbf{r}}\mathbf{1})):\boldsymbol{\nabla}\mathbf{v}_{\mathbf{r}} - \boldsymbol{\nabla}\cdot(\mathcal{G}^{-1}_{\mathbf{r}}\mathbf{J}^{q}_{\mathbf{r}}(z)) \\
&+\sum_{\alpha}(\mathcal{G}^{-1}_{\mathbf{r}}\mathbf{J}^{\alpha}_{\mathbf{r}}(z))\cdot\overline{\mathbf{F}}^{\alpha}_{\mathbf{r}}(z).
\end{aligned}
$$

We have introduced the following microscopic fluxes:

$$
\begin{aligned}
\mathbf{J}^{\alpha}_{\mathbf{r}}(z) =& \frac{\mathbf{g}^{\alpha}_{\mathbf{r}}(z)}{m_\alpha}, \\
\hat{\boldsymbol{\sigma}}_{\mathbf{r}}(z) =& \sum_{\alpha}\sum_{i_\alpha}\mathbf{p}_{i_\alpha}\mathbf{v}_{i_\alpha}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha}) \\
&+\frac{1}{2}\sum_{\alpha\beta}\sum_{i_\alpha j_\beta}\hat{\mathbf{F}}_{i_\alpha j_\beta}\mathbf{q}_{i_\alpha j_\beta}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha}), \qquad (137) \\
\hat{\mathbf{J}}^{q}_{\mathbf{r}}(z) =& \sum_{\alpha}\sum_{i_\alpha}\left(\frac{\mathbf{p}^2_{i_\alpha}}{2m_\alpha}+\hat{\phi}_{i_\alpha}\right)\mathbf{v}_{i_\alpha}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha}) \\
&+\frac{1}{4}\sum_{\alpha\beta}\sum_{i_\alpha j_\beta}(\mathbf{v}_{i_\alpha}+\mathbf{v}_{j_\beta})\hat{\mathbf{F}}_{i_\alpha j_\beta}\mathbf{q}_{i_\alpha j_\beta}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha}).
\end{aligned}
$$

Here $\mathbf{J}^{\alpha}_{\mathbf{r}}(z)$ is the microscopic mass flux, $\hat{\boldsymbol{\sigma}}_{\mathbf{r}}(z)$ is the microscopic stress tensor, and $\hat{\mathbf{J}}^{q}_{\mathbf{r}}(z)$ is the microscopic heat flux. It is quite remarkable that in these microscopic fluxes, only the short-range part of the force appears. The long-range part of the forces disappears when computing the constrained average of these fluxes.

We proceed now to the explicit calculation of the elements of the irreversible matrix M defined in Eq. (49). This matrix will have the following form:

$$
M_{\mathbf{r}\mathbf{r}'} = \begin{pmatrix} M^{\alpha\beta}_{\mathbf{r}\mathbf{r}'} & M^{\alpha\mathbf{g}}_{\mathbf{r}\mathbf{r}'} & M^{\alpha\hat{\epsilon}}_{\mathbf{r}\mathbf{r}'} \\ M^{\mathbf{g}\beta}_{\mathbf{r}\mathbf{r}'} & M^{\mathbf{g}\mathbf{g}}_{\mathbf{r}\mathbf{r}'} & M^{\mathbf{g}\hat{\epsilon}}_{\mathbf{r}\mathbf{r}'} \\ M^{\hat{\epsilon}\beta}_{\mathbf{r}\mathbf{r}'} & M^{\hat{\epsilon}\mathbf{g}}_{\mathbf{r}\mathbf{r}'} & M^{\hat{\epsilon}\hat{\epsilon}}_{\mathbf{r}\mathbf{r}'} \end{pmatrix}, \qquad (138)
$$

where every element is a Green–Kubo formula involving the time integral of a correlation function as in Eq. (49). We only need to consider the six elements of the upper triangular part, because M is symmetric. The first element $M^{\alpha\beta}_{\mathbf{r}\mathbf{r}'}$ involves the following correlation:

$$
\begin{aligned}
&\langle\delta iLn^{\alpha}_{\mathbf{r}}\exp\{QiLt\}\delta iLn^{\beta}_{\mathbf{r}'}\rangle^x \\
&\quad=\nabla\nabla'\langle\mathcal{G}^{-1}_{\mathbf{r}}\mathbf{J}^{\alpha}_{\mathbf{r}}\exp\{QiLt\}\mathcal{G}^{-1}_{\mathbf{r}'}\mathbf{J}^{\beta}_{\mathbf{r}'}\rangle^x, \qquad (139)
\end{aligned}
$$

where $\nabla' = \partial/\partial\mathbf{r}'$. We will make in the following the assumption that the dynamics represented by $\exp QiLt$ in the Green–Kubo expression for the matrix M can be substituted by $\exp Qi\hat{L}t$, as if only the short-range part of the potential was present. The intuitive reasoning behind this approximation is that the long-range forces are slowly varying (as they essentially depend on the density field, which is a slow variable) in the time scale of the correlation times of the micro-

scopic fluxes. Then the projected dynamics systematically subtracts these slowly varying forces from the dynamics. From now on, every instance of a time dependence will be assumed to be generated by the hard-core dynamics only.

Another approximation that we will take is to neglect the correlation of the projected fluxes of different cell. This amounts to neglect nonlocal effects due to the transport coefficients in the final hydrodynamic equations. Therefore, the constrained average in Eq. (139) is over a local function, and we can apply Eq. (102) in order to compute the constrained average. We end up with

$$\langle \delta iLn_{\mathbf{r}}^{\alpha}\delta iLn_{\mathbf{r}}^{\beta}(t)\rangle^{x}=\nabla\nabla'\delta_{\mathbf{rr}'}\frac{1}{\mathcal{V}_{\mathbf{r}}}\langle \mathbf{V}^{\alpha}\mathbf{V}^{\beta}(t)\rangle_{\mathbf{r}}^{\mathrm{eq}}, \tag{140}$$

where $\mathcal{V}_{\mathbf{r}}$ is the volume of the cell labeled with $\mathbf{r}$ and we have introduced the average velocity of species α as

$$\mathbf{V}^{\alpha}=\sum_{i_{\alpha}}^{N^{\alpha}}\mathbf{v}_{i_{\alpha}}. \tag{141}$$

The equilibrium ensemble is isotropic and this means that the above correlation function is isotropic too, that is,

$$\langle \delta iLn_{\mathbf{r}}^{\alpha}\delta iLn_{\mathbf{r}}^{\beta}(t)\rangle^{x}=\nabla\cdot\nabla'\delta_{\mathbf{rr}'}\frac{1}{3\mathcal{V}_{\mathbf{r}}}\langle \mathbf{V}^{\alpha}\cdot\mathbf{V}^{\beta}(t)\rangle_{\mathbf{r}}^{\mathrm{eq}}. \tag{142}$$

The corresponding Green–Kubo expression that appears in the matrix M will be

$$M_{\mathbf{rr}'}^{\alpha\beta}=\nabla\cdot\nabla(\delta_{\mathbf{rr}'}D_{\mathbf{r}}^{\alpha\beta}\hat{T}_{\mathbf{r}}), \tag{143}$$

where we have introduced the diffusion coefficients through[19,20]

$$D_{\mathbf{r}}^{\alpha\beta}=\frac{1}{2k_B\hat{T}_{\mathbf{r}}}\frac{1}{\mathcal{V}_{\mathbf{r}}}\int_{-\infty}^{\infty}dt\frac{1}{3}\langle \mathbf{V}^{\alpha}\cdot\mathbf{V}^{\beta}(t)\rangle_{\mathbf{r}}^{\mathrm{eq}}. \tag{144}$$

Note that the equilibrium ensemble involved in Eq. (144) is a microcanonical one at rest. This means that $\Sigma_{\alpha}m_{\alpha}\mathbf{V}_{\alpha}$, which is the total momentum of the system, is exactly zero at all times. For this reason, we have that not all the diffusion coefficients are independent, but

$$\sum_{\alpha}m_{\alpha}D_{\mathbf{r}}^{\alpha\beta}=0. \tag{145}$$

The next element $M_{\mathbf{rr}'}^{\alpha\mathbf{g}}$ involves the correlation $\langle \delta iLn_{\mathbf{r}}^{\alpha}\exp QiLt\delta iL\mathbf{g}_{\mathbf{r}'}\rangle^{x}$. Under the same approximations used above, we can write

$$\langle \delta iLn_{\mathbf{r}}^{\alpha}\delta iL\mathbf{g}_{\mathbf{r}'}(t)\rangle^{x}=\nabla\nabla'\delta_{\mathbf{rr}'}\frac{1}{\mathcal{V}_{\mathbf{r}}}\langle \mathbf{V}^{\alpha}(\hat{\boldsymbol{\Sigma}}(t)-\hat{P}_{\mathbf{r}}\mathbf{1})\rangle_{\mathbf{r}}^{\mathrm{eq}}, \tag{146}$$

where the macroscopic stress tensor is given by

$$\hat{\boldsymbol{\Sigma}}=\sum_{\alpha}\sum_{i_{\alpha}}^{N^{\alpha}}\mathbf{p}_{i_{\alpha}}\mathbf{v}_{i_{\alpha}}+\frac{1}{2}\sum_{\alpha\beta}\sum_{i_{\alpha}j_{\beta}}^{N^{\alpha}N^{\beta}}\hat{\mathbf{F}}_{i_{\alpha}j_{\beta}}\mathbf{q}_{i_{\alpha}j_{\beta}}. \tag{147}$$

Due to the isotropy of the equilibrium ensemble, the above correlation, which is a third-order tensor, should vanish and then $M_{\mathbf{rr}'}^{\alpha\mathbf{g}}=0$.

The next element to be computed is $M_{\mathbf{rr}'}^{\alpha\epsilon}$ which involves the correlation

$$\langle \delta iLn_{\mathbf{r}}^{\alpha}\delta iL\hat{\boldsymbol{\epsilon}}_{\mathbf{r}'}(t)\rangle^{x}=\nabla\nabla'\delta_{\mathbf{rr}'}\frac{1}{\mathcal{V}_{\mathbf{r}}}\langle \mathbf{V}^{\alpha}\hat{\mathbf{Q}}(t)\rangle_{\mathbf{r}}^{\mathrm{eq}}-\nabla\delta_{\mathbf{rr}'}\sum_{\beta}\frac{1}{\mathcal{V}_{\mathbf{r}}}\langle \mathbf{V}^{\alpha}\mathbf{V}^{\beta}(t)\rangle_{\mathbf{r}}^{\mathrm{eq}}\overline{\mathbf{F}}_{\mathbf{r}}^{\beta}, \tag{148}$$

where we have introduced the macroscopic heat flux

$$\hat{\mathbf{Q}}=\sum_{\alpha}\sum_{i_{\alpha}}^{N^{\alpha}}\left(\frac{\mathbf{p}_{i_{\alpha}}^{2}}{2m_{\alpha}}+\hat{\phi}_{i_{\alpha}}\right)\mathbf{v}_{i_{\alpha}}+\frac{1}{4}\sum_{\alpha\beta}\sum_{i_{\alpha}j_{\beta}}^{N^{\alpha}N^{\beta}}(\mathbf{v}_{i_{\alpha}}+\mathbf{v}_{j_{\beta}})\hat{\mathbf{F}}_{i_{\alpha}j_{\beta}}\mathbf{q}_{i_{\alpha}j_{\beta}}. \tag{149}$$

In Eq. (148) we have omitted a third-order tensor that vanishes by isotropy. The corresponding element of the matrix M will be

$$M_{\mathbf{rr}'}^{\alpha\hat{\epsilon}}=\nabla\cdot\nabla'(\delta_{\mathbf{rr}'}S_{\mathbf{r}}^{\alpha}\hat{T}_{\mathbf{r}}^{2})-\nabla\delta_{\mathbf{rr}'}\sum_{\beta}D_{\mathbf{r}}^{\alpha\beta}\overline{\mathbf{F}}_{\mathbf{r}}^{\beta}, \tag{150}$$

where the cross coefficient $S_{\mathbf{r}}^{\alpha}$ is defined through the Green–Kubo formula[19,20]

$$S_{\mathbf{r}}^{\alpha}=\frac{1}{2k_B\hat{T}_{\mathbf{r}}^{2}}\frac{1}{\mathcal{V}_{\mathbf{r}}}\int_{-\infty}^{\infty}dt\frac{1}{3}\langle \mathbf{V}^{\alpha}\cdot\hat{\mathbf{Q}}(t)\rangle_{\mathbf{r}}^{\mathrm{eq}}. \tag{151}$$

Again, we have the identity

$$\sum_{\alpha}m_{\alpha}S_{\mathbf{r}}^{\alpha}=0 \tag{152}$$

due to momentum conservation.

The next correlation is

$$\langle \delta iL\mathbf{g}_{\mathbf{r}}\delta iL\mathbf{g}_{\mathbf{r}'}(t)\rangle^{x}=\nabla\nabla'\delta_{\mathbf{rr}'}\frac{1}{\mathcal{V}_{\mathbf{r}}}\langle \hat{\boldsymbol{\Sigma}}\hat{\boldsymbol{\Sigma}}(t)\rangle_{\mathbf{r}}^{\mathrm{eq}}, \tag{153}$$

where we have omitted some third-order tensors that vanish by isotropy. The corresponding element of the matrix M is an isotropic fourth-order tensor

$$M_{\mathbf{r}}^{\mathbf{gg}}=\nabla\nabla':\boldsymbol{\Theta}_{\mathbf{r}}\hat{T}_{\mathbf{r}}\delta_{\mathbf{rr}'}, \tag{154}$$

where the isotropic fourth-order tensor is given by

$$\boldsymbol{\Theta}_{\mathbf{r}}^{\mu\nu\mu'\nu'}=\hat{\eta}_{\mathbf{r}}(\delta^{\mu\mu'}\delta^{\nu\nu'}+\delta^{\mu\nu'}\delta^{\nu\mu'})+(\hat{\zeta}_{\mathbf{r}}-\tfrac{2}{3}\hat{\eta}_{\mathbf{r}})\delta^{\mu\nu}\delta^{\mu'\nu'}, \tag{155}$$

where the usual Green–Kubo expressions for the shear η and bulk ζ viscosities appear:

$$\hat{\eta}_{\mathbf{r}}=\frac{1}{2k_B\hat{T}_{\mathbf{r}}}\frac{1}{\mathcal{V}_{\mathbf{r}}}\int_{-\infty}^{\infty}dt\langle \hat{\boldsymbol{\Sigma}}^{xy}\hat{\boldsymbol{\Sigma}}^{xy}(t)\rangle_{\mathbf{r}}^{\mathrm{eq}},$$
$$\hat{\zeta}_{\mathbf{r}}=\frac{1}{2k_B\hat{T}_{\mathbf{r}}}\frac{1}{\mathcal{V}_{\mathbf{r}}}\int_{\infty}^{-\infty}dt\langle(\hat{\boldsymbol{\Sigma}}^{xx}-\hat{P}_{\mathbf{r}})(\hat{\boldsymbol{\Sigma}}^{xx}-\hat{P}_{\mathbf{r}})(t)\rangle_{\mathbf{r}}^{\mathrm{eq}}. \tag{156}$$

The next correlation is

$$\langle \delta iL\mathbf{g}_{\mathbf{r}}\delta iL\hat{\epsilon}_{\mathbf{r}'}(t)\rangle^{x}=\nabla\left(\delta_{\mathbf{r}\mathbf{r}'}\frac{1}{\mathcal{V}_{\mathbf{r}}}\langle\hat{\mathbf{\Sigma}}\hat{\mathbf{\Sigma}}(t)\rangle_{\mathbf{r}}^{\mathrm{eq}}:\nabla\mathbf{v}_{\mathbf{r}}\right), \quad (157)$$

where we have neglected again some third-order tensors. The corresponding element of the matrix M is

$$M_{\mathbf{r}}^{\mathbf{g}\hat{\epsilon}}=\nabla(\delta_{\mathbf{r}\mathbf{r}'}\hat{T}_{\mathbf{r}}\mathbf{\Theta}:\nabla\mathbf{v}_{\mathbf{r}}). \quad (158)$$

The last correlation is given by

$$\begin{aligned}\langle \delta iL\hat{\epsilon}_{\mathbf{r}}\delta iL\hat{\epsilon}_{\mathbf{r}'}(t)\rangle^{x}&=\nabla\nabla'\left(\delta_{\mathbf{r}\mathbf{r}'}\frac{1}{\mathcal{V}_{\mathbf{r}}}\langle\hat{\mathbf{Q}}\hat{\mathbf{Q}}(t)\rangle_{\mathbf{r}}^{\mathrm{eq}}\right)+\delta_{\mathbf{r}\mathbf{r}'}\frac{1}{\mathcal{V}_{\mathbf{r}}}\nabla\mathbf{v}_{\mathbf{r}}:\langle\hat{\mathbf{\Sigma}}\mathbf{\Sigma}(t)\rangle_{\mathbf{r}}^{\mathrm{eq}}:\nabla\mathbf{v}_{\mathbf{r}}\\&+\delta_{\mathbf{r}\mathbf{r}'}\frac{1}{\mathcal{V}_{\mathbf{r}}}\sum_{\alpha\beta}\langle\mathbf{V}^{\alpha}\mathbf{V}^{\beta}(t)\rangle_{\mathbf{r}}^{\mathrm{eq}}\overline{\mathbf{F}}_{\mathbf{r}}^{\alpha}\overline{\mathbf{F}}_{\mathbf{r}}^{\beta}\\&-\nabla\left(\sum_{\alpha}\delta_{\mathbf{r}\mathbf{r}'}\langle\mathbf{V}^{\alpha}\hat{\mathbf{Q}}(t)\rangle_{\mathbf{r}}^{\mathrm{eq}}\overline{\mathbf{F}}_{\mathbf{r}}^{\alpha}\right)\\&-\nabla'\left(\sum_{\alpha}\delta_{\mathbf{r}\mathbf{r}'}\langle\hat{\mathbf{Q}}\mathbf{V}^{\alpha}(t)\rangle_{\mathbf{r}}^{\mathrm{eq}}\overline{\mathbf{F}}_{\mathbf{r}}^{\alpha}\right), \quad (159)\end{aligned}$$

and the corresponding element of the matrix M is

$$\begin{aligned}M_{\mathbf{r}\mathbf{r}'}^{\hat{\epsilon}\hat{\epsilon}}&=\nabla\cdot\nabla'(\hat{\kappa}_{\mathbf{r}}\hat{T}_{\mathbf{r}}^{2}\delta_{\mathbf{r}\mathbf{r}'})+\delta_{\mathbf{r}\mathbf{r}'}\nabla\mathbf{v}_{\mathbf{r}}:\mathbf{\Theta}_{\mathbf{r}}:\nabla\mathbf{v}_{\mathbf{r}}\hat{T}_{\mathbf{r}}-(\nabla+\nabla')\\&\times\left(\delta_{\mathbf{r}\mathbf{r}'}\sum_{\alpha}S_{\mathbf{r}}^{\alpha}\overline{\mathbf{F}}_{\mathbf{r}}^{\alpha}\right)+\delta_{\mathbf{r}\mathbf{r}'}\sum_{\alpha\beta}D_{\mathbf{r}}^{\alpha\beta}\overline{\mathbf{F}}_{\mathbf{r}}^{\alpha}\cdot\overline{\mathbf{F}}_{\mathbf{r}}^{\alpha}\hat{T}_{\mathbf{r}}, \quad (160)\end{aligned}$$

where the usual Green–Kubo expression for the thermal conductivity $\hat{\kappa}$ has been introduced:

$$\hat{\kappa}_{\mathbf{r}}=\frac{1}{2k_{B}\hat{T}_{\mathbf{r}}^{2}}\frac{1}{\mathcal{V}_{\mathbf{r}}}\int_{-\infty}^{\infty}dt\frac{1}{3}\langle\hat{\mathbf{Q}}\cdot\hat{\mathbf{Q}}(t)\rangle_{\mathbf{r}}^{\mathrm{eq}}. \quad (161)$$

By collecting all the elements of the matrix M we note that we can write it as the sum of two matrices $M_{\mathbf{r}\mathbf{r}'}=D_{\mathbf{r}\mathbf{r}'}+H_{\mathbf{r}\mathbf{r}'}$ where $D_{\mathbf{r}\mathbf{r}'}$ contains all those transport coefficients related to diffusion of mass and heat, and $H_{\mathbf{r}\mathbf{r}'}$ contains the viscosity transport coefficients. More explicitly, we can write for the matrices $D_{\mathbf{r}\mathbf{r}'}$ and $H_{\mathbf{r}\mathbf{r}'}$:

$$D_{\mathbf{r}\mathbf{r}'}=\begin{pmatrix}\nabla\cdot\nabla'(\delta_{\mathbf{r}\mathbf{r}'}D_{\mathbf{r}}^{\alpha\beta}\hat{T}_{\mathbf{r}}) & 0 & -\nabla\cdot\left(\delta_{\mathbf{r}\mathbf{r}'}\sum_{\beta}D_{\mathbf{r}}^{\alpha\beta}\hat{T}_{\mathbf{r}}\overline{\mathbf{F}}_{\mathbf{r}}^{\beta}\right)+\nabla\cdot\nabla'(\delta_{\mathbf{r}\mathbf{r}'}S_{\mathbf{r}}^{\alpha}\hat{T}_{\mathbf{r}}^{2})\\ 0 & 0 & 0\\ -\nabla'\cdot\left(\delta_{\mathbf{r}\mathbf{r}'}\sum_{\beta}D_{\mathbf{r}}^{\alpha\beta}\hat{T}_{\mathbf{r}}\overline{\mathbf{F}}_{\mathbf{r}}^{\beta}\right)+\nabla\cdot\nabla'(\delta_{\mathbf{r}\mathbf{r}'}S_{\mathbf{r}}^{\alpha}\hat{T}_{\mathbf{r}}^{2}) & 0 & \sum_{\alpha\beta}\delta_{\mathbf{r}\mathbf{r}'}D_{\mathbf{r}}^{\alpha\beta}\hat{T}_{\mathbf{r}}\overline{\mathbf{F}}_{\mathbf{r}}^{\alpha}\cdot\overline{\mathbf{F}}_{\mathbf{r}}^{\beta}-(\nabla+\nabla')\cdot\left(\sum_{\alpha}S_{\mathbf{r}}^{\alpha}\delta_{\mathbf{r}\mathbf{r}'}\hat{T}_{\mathbf{r}}^{2}\overline{\mathbf{F}}_{\mathbf{r}}^{\alpha}\right)+\nabla\cdot\nabla'(\delta_{\mathbf{r}\mathbf{r}'}\hat{\kappa}_{\mathbf{r}}\hat{T}_{\mathbf{r}}^{2})\end{pmatrix}, \quad (162)$$

$$H_{\mathbf{r}\mathbf{r}'}=\begin{pmatrix}0 & 0 & 0\\ 0 & (\nabla'\nabla+\mathbf{1}\nabla\cdot\nabla')\hat{\eta}_{\mathbf{r}}\hat{T}_{\mathbf{r}}\delta_{\mathbf{r}\mathbf{r}'}+\nabla\nabla'(\hat{\zeta}_{\mathbf{r}}-\frac{2}{3}\eta_{\mathbf{r}})\hat{T}_{\mathbf{r}}\delta_{\mathbf{r}\mathbf{r}'} & \nabla\hat{\eta}_{\mathbf{r}}\hat{T}_{\mathbf{r}}\dot{\gamma}_{\mathbf{r}}\delta_{\mathbf{r}\mathbf{r}'}+\nabla(\hat{\zeta}_{\mathbf{r}}-\frac{2}{3}\eta_{\mathbf{r}})\hat{T}_{\mathbf{r}}\mathrm{tr}\dot{\gamma}\delta_{\mathbf{r}\mathbf{r}'}\\ 0 & \nabla'\hat{\eta}_{\mathbf{r}}\hat{T}_{\mathbf{r}}\dot{\gamma}_{\mathbf{r}}\delta_{\mathbf{r}\mathbf{r}'}+\nabla'(\hat{\zeta}_{\mathbf{r}}-\frac{2}{3}\eta_{\mathbf{r}})\hat{T}_{\mathbf{r}}\mathrm{tr}\dot{\gamma}\delta_{\mathbf{r}\mathbf{r}'} & \frac{1}{2}\hat{\eta}_{\mathbf{r}}\hat{T}_{\mathbf{r}}\dot{\gamma}_{\mathbf{r}}:\dot{\gamma}_{\mathbf{r}}\delta_{\mathbf{r}\mathbf{r}'}+(\hat{\zeta}_{\mathbf{r}}-\frac{2}{3}\eta_{\mathbf{r}})\hat{T}_{\mathbf{r}}(\mathrm{tr}\dot{\gamma})^{2}\delta_{\mathbf{r}\mathbf{r}'}\end{pmatrix}, \quad (163)$$

where $\dot{\gamma}_{\mathbf{r}}=\nabla\mathbf{v}_{\mathbf{r}}+(\nabla\mathbf{v}_{\mathbf{r}})^{T}$ is the symmetrized velocity gradient tensor.

It is possible to write the matrix $M_{\mathbf{r}\mathbf{r}'}$ in a more compact way. Eqs. (136) suggest to introduce the following fluxes:

$$\begin{aligned}\delta iLn_{\mathbf{r}}^{\alpha}&=-\nabla\tilde{\mathbf{J}}_{\mathbf{r}}^{\alpha},\\ \delta iL\mathbf{g}_{\mathbf{r}}&=-\nabla\tilde{\boldsymbol{\sigma}}_{\mathbf{r}},\\ \delta iL\hat{\epsilon}_{\mathbf{r}}&=\tilde{\boldsymbol{\sigma}}_{\mathbf{r}}:\nabla\mathbf{v}_{\mathbf{r}}-\nabla\tilde{\mathbf{Q}}_{\mathbf{r}}+\sum_{\alpha}\tilde{\mathbf{J}}_{\mathbf{r}}^{\alpha}\cdot\overline{\mathbf{F}}_{\mathbf{r}}^{\alpha},\end{aligned} \quad (164)$$

where we have introduced the "stochastic" mass flux $\tilde{\mathbf{J}}_{\mathbf{r}}^{\alpha}$, the "stochastic" stress tensor $\tilde{\boldsymbol{\sigma}}_{\mathbf{r}}$, and the "stochastic" flux $\tilde{\mathbf{Q}}_{\mathbf{r}}$. These "stochastic" fluxes are actually phase functions with definite microscopic expressions. They are not stochastic at all but deterministic. We will understand the time evolution of δiLX to be generated by the projected dynamics, that is, $\delta iLX(t)=\exp\{Qilt\}\delta iLX$. Of course, even though the projected dynamics is deterministic, the correlation times of the projected currents $\delta iLX(t)$ are very short as compared with the time scales of the relevant variables. This is only possible if these functions change rapidly in time, allowing for a modelization in terms of random noise.

Note that we can write Eqs. (164) in compact form as follows:

$$\begin{pmatrix}\delta iLn_{\mathbf{r}}^{\alpha}\\ \delta iL\mathbf{g}_{\mathbf{r}}\\ \delta iL\hat{\epsilon}_{\mathbf{r}}\end{pmatrix}=\begin{pmatrix}-\nabla_{\mathbf{r}} & 0 & 0\\ 0 & -\nabla_{\mathbf{r}} & 0\\ \overline{\mathbf{F}}_{\mathbf{r}}^{\alpha} & \nabla_{\mathbf{r}}\mathbf{v}_{\mathbf{r}} & -\nabla_{\mathbf{r}}\end{pmatrix}\begin{pmatrix}\tilde{\mathbf{J}}_{\mathbf{r}}^{\alpha}\\ \tilde{\boldsymbol{\sigma}}_{\mathbf{r}}\\ \tilde{\mathbf{Q}}_{\mathbf{r}}\end{pmatrix}. \quad (165)$$

In this way, we have separated the vector of projected currents into two parts, one which is strictly kinematic and that depends only on the relevant variables and another that contains the "stochastic" fluxes. These fluxes are, actually, what enters into the definition of the transport coefficients through the Green–Kubo expressions.

It is now quite simple to rewrite the Green–Kubo expression (49) for M in the form

$$M_{\mathbf{r}\mathbf{r}'}=\begin{pmatrix} -\nabla_{\mathbf{r}} & 0 & 0 \\ 0 & -\nabla_{\mathbf{r}} & 0 \\ \overline{\mathbf{F}}^{\alpha}_{\mathbf{r}} & \nabla_{\mathbf{r}}\mathbf{v}_{\mathbf{r}} & -\nabla_{\mathbf{r}} \end{pmatrix} \begin{pmatrix} D^{\alpha\beta}_{\mathbf{r}}\hat{T}_{\mathbf{r}} & 0 & S^{\alpha}_{\mathbf{r}}\hat{T}^2_{\mathbf{r}} \\ 0 & \theta_{\mathbf{r}}\hat{T}_{\mathbf{r}} & 0 \\ S^{\alpha}_{\mathbf{r}}\hat{T}^2_{\mathbf{r}} & 0 & \kappa_{\mathbf{r}}\hat{T}^2_{\mathbf{r}} \end{pmatrix} \times \begin{pmatrix} -\nabla_{\mathbf{r}'} & 0 & \overline{\mathbf{F}}^{\alpha}_{\mathbf{r}'} \\ 0 & -\nabla_{\mathbf{r}'} & \nabla_{\mathbf{r}'}\mathbf{v}_{\mathbf{r}'} \\ 0 & 0 & -\nabla_{\mathbf{r}'} \end{pmatrix} \delta_{\mathbf{r}\mathbf{r}'}. \tag{166}$$

The fact that the M matrix can be decomposed as $M=CDC^T$ in terms of a purely mechanic matrix C and purely thermodynamic matrix D has been discovered in Refs. 32. From the microscopic example presented here, the splitting can be traced back to the particular splitting of the projected currents δiLX in terms of the stochastic fluxes that enter into the definition of the Green–Kubo expression for the matrix M. It is apparent that the symmetry of the the matrix M is ensured if D is symmetric and that the positive semidefinite character of D also ensures that M is positive semidefinite. We discuss the positive semidefinite character of D in Sec. V. As a final remark, we note that one of the merits of the $M=CDC^T$ decomposition is that it facilitates the task of constructing new models for complex fluids. We see, therefore, that for macroscopic modeling purposes, it may be very convenient to follow the ''noise route to dissipation,'' as we can call it, where one first computes the time derivative of the microscopically defined relevant variables, identifies the ''stochastic fluxes'' that will produce transport coefficients in the Green–Kubo formula, and then constructs the matrix M which, automatically, will have the CDC^T structure.

We are now in position of writing the irreversible part of the dynamics $M\nabla S$ by multiplying the matrix M with the functional derivatives of the entropy in Eq. (94) and integrating over $\mathbf{r}'$. The matrix H will produce the well-known terms of the Navier–Stokes equations that contain the viscosity coefficients. We write with some detail the part of the equations that involve the diffusion of mass and heat:

$$\begin{aligned} \partial_t n^{\alpha}|_{\mathrm{diff}} &= \nabla\left(\sum_{\beta} D^{\alpha\beta}_{\mathbf{r}}\hat{T}_{\mathbf{r}}\nabla\left(\frac{\hat{\mu}^{\beta}_{\mathbf{r}}}{\hat{T}_{\mathbf{r}}}\right)\right)-\nabla\left(S^{\alpha}_{\mathbf{r}}\hat{T}^2_{\mathbf{r}}\nabla\left(\frac{1}{\hat{T}_{\mathbf{r}}}\right)\right) \\ &\quad -\nabla\left(\sum_{\beta} D^{\alpha\beta}_{\mathbf{r}}\overline{\mathbf{F}}^{\beta}_{\mathbf{r}}\right), \\ \partial_t \hat{\epsilon}|_{\mathrm{diff}} &= \nabla\left(\sum_{\alpha} S^{\alpha}_{\mathbf{r}}\hat{T}^2_{\mathbf{r}}\nabla\left(\frac{\hat{\mu}^{\alpha}_{\mathbf{r}}}{\hat{T}_{\mathbf{r}}}\right)\right)-\nabla\left(\hat{\kappa}_{\mathbf{r}}\hat{T}^2_{\mathbf{r}}\nabla\left(\frac{1}{\hat{T}_{\mathbf{r}}}\right)\right) \\ &\quad -\sum_{\alpha\beta}\left[\hat{T}_{\mathbf{r}}\nabla\left(\frac{\hat{\mu}^{\alpha}_{\mathbf{r}}}{\hat{T}_{\mathbf{r}}}\right)-\overline{\mathbf{F}}^{\alpha}_{\mathbf{r}}\right]D^{\alpha\beta}_{\mathbf{r}}\overline{\mathbf{F}}^{\beta}_{\mathbf{r}} \\ &\quad -\nabla\left(\sum_{\alpha} S^{\alpha}_{\mathbf{r}}\overline{\mathbf{F}}^{\alpha}_{\mathbf{r}}\hat{T}_{\mathbf{r}}\right)-\sum_{\alpha} S^{\alpha}_{\mathbf{r}}\overline{\mathbf{F}}^{\alpha}_{\mathbf{r}}\nabla\hat{T}_{\mathbf{r}}. \end{aligned} \tag{167}$$

By collecting Eqs. (167), with the usual viscous terms, and the reversible part of the dynamics in Eqs. (120)–(125), we obtain the final hydrodynamic equations for a phase separating mixture given in Eqs. (6).

V. POSITIVE TRANSPORT MATRIX

Although we know in advance that the transport matrix is positive, we check under which conditions the matrix D introduced in Eq. (162) is positive semidefinite. For the sake of simplicity, we study the binary mixture case. We double contract that matrix D with an arbitrary vector function $G_{\mathbf{r}}=(G^A_{\mathbf{r}},G^B_{\mathbf{r}},G^g_{\mathbf{r}},G^e_{\mathbf{r}})$, understanding that a contraction of the continuous matrix $M_{\mathbf{r}\mathbf{r}'}$ involves integrals over the continuous indices. After some algebra that involves integration by parts one easily arrives at the following expression:

$$\begin{aligned} &\int d\mathbf{r}\, d\mathbf{r}'\; G_{\mathbf{r}}M_{\mathbf{r}\mathbf{r}'}G_{\mathbf{r}'} \\ &= \int d\mathbf{r}\; \hat{T}(\nabla G^A_{\mathbf{r}}+\overline{F}^A_{\mathbf{r}}G^{\epsilon}_{\mathbf{r}},\nabla G^B_{\mathbf{r}}+\overline{F}^B_{\mathbf{r}}G^{\epsilon}_{\mathbf{r}},\nabla G^{\epsilon}_{\mathbf{r}}) \\ &\quad \times\begin{pmatrix} D^{AA}_{\mathbf{r}} & D^{AB}_{\mathbf{r}} & \hat{T}S^A_{\mathbf{r}} \\ D^{BA}_{\mathbf{r}} & D^{BB}_{\mathbf{r}} & \hat{T}S^B_{\mathbf{r}} \\ \hat{T}S^A_{\mathbf{r}} & \hat{T}S^B_{\mathbf{r}} & \hat{T}\hat{\kappa}_{\mathbf{r}} \end{pmatrix}\begin{pmatrix} \nabla G^A_{\mathbf{r}}+\overline{F}^A_{\mathbf{r}}G^{\epsilon}_{\mathbf{r}} \\ \nabla G^B_{\mathbf{r}}+\overline{F}^B_{\mathbf{r}}G^{\epsilon}_{\mathbf{r}} \\ \nabla G^{\epsilon}_{\mathbf{r}} \end{pmatrix}. \end{aligned} \tag{168}$$

It is apparent that in order for this quantity to be positive (or zero), we need that the inner matrix be positive *semi*definite. Note that the vector $(m_A,m_B,0)$ is an eigenvector of the above matrix with null eigenvalue, due to Eqs. (145) and (152). Actually, by using these equations we can write the matrix as

$$\begin{pmatrix} D & -rD & \hat{T}S \\ -rD & r^2D & -r\hat{T}S \\ \hat{T}S & -r\hat{T}S & \hat{T}\hat{\kappa} \end{pmatrix}, \tag{169}$$

where $r=m_A/m_B$ is the ratio of molecular mass of the two species, $D=D^{AA}_{\mathbf{r}}$, and $S=S^A_{\mathbf{r}}$. By multiplying Eq. (169) by the right and the left with an arbitrary vector (x,y,z) we obtain

$$\begin{aligned} &(x,y,z)\begin{pmatrix} D & -rD & \hat{T}S \\ -rD & r^2D & -r\hat{T}S \\ \hat{T}S & -r\hat{T}S & \hat{T}\hat{\kappa} \end{pmatrix}\begin{pmatrix} x \\ y \\ Z \end{pmatrix} \\ &= D(x-ry)^2+\hat{T}S2(x-ry)z+\hat{T}\hat{\kappa}z^2. \end{aligned} \tag{170}$$

For this quantity to be positive for arbitrary x,y,z we need D and $\hat{\kappa}$ to be positive. If we define $x'=D^{1/2}(x-ry)$, $z'=S/D^{1/2}z$, the quadratic form (170) becomes

$$(x'+z')^2+\left(\frac{D\hat{\kappa}}{\hat{T}S^2}-1\right)z'^2, \tag{171}$$

which will be positive if and only if $D\hat{\kappa}>\hat{T}S^2$.

The conditions $D>0$, $\hat{\kappa}>0$, and $D\hat{\kappa}>\hat{T}S^2$ are actually the conditions for the following matrix to be definite positive:

$$\begin{pmatrix} D & \hat{T}S \\ \hat{T}S & \hat{T}\hat{\kappa} \end{pmatrix}. \tag{172}$$

By forming a quadratic form with an arbitrary vector (x,y) we can write

$$(x,y)\begin{pmatrix} D & \hat{T}S \\ \hat{T}S & \hat{T}\hat{\kappa} \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix}$$

$$= \frac{1}{2k_B\hat{T}}\int_{-\infty}^{\infty}\langle (xV^A+yQ)(xV^A+yQ)(t)\rangle. \qquad (173)$$

The right-hand side of this equation is the time integral of an autocorrelation function. By recalling the Wiener–Kinchin theorem that states that the Fourier transform of a stationary autocorrelation function is positive,[8] we conclude that the quadratic form is positive or, in other words, that the matrix (172) is a positive matrix.[29]

ACKNOWLEDGMENTS

One of the authors (P.E.) would like to thank Nicos Martys for useful discussions at a very early stage of this work. Partial financial support from Ministerio de Ciencia y Tecnología, Grant No. BFM2001-0290, is acknowledged. C.T. acknowledges financial support of the European Community project ICOPAC.

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